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ENVIRO

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Information for

Problem

Spills

ACETIC ANHYDRIDE

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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ACETIC ANHYDRIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUAL

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

ACETIC ANHYDRIDE ($CH_3CO\text{-}O\text{-}COCH_3$)

Colourless, watery liquid with a strong vinegar-like odour

SYNONYMS

Acetic Oxide, Ethanoic Anhydride, Acetic Acid Anhydride, Acetyoxide, Anhydride Acétique (Fr.)

IDENTIFICATION NUMBERS

UN No. 1715; CAS No. 108-24-7; OHM-TADS No. 7216567; STCC No. 4931304

GRADES & PURITIES

Pure: >99.0 percent
Technical: 78-98.5 percent

IMMEDIATE CONCERNS

Fire: Combustible. Irritating vapours are generated when heated

Human Health: Corrosive to tissue upon inhalation, ingestion and contact

Environmental: Harmful to aquatic life in low concentrations

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid
Boiling Point: 139.6°C
Melting Point: -73.1°C
Flammability: combustible
Flash Point: 49°C (CC)
Vapour Pressure: 0.4 kPa (20°C)
Density: 1.082 g/mL (20°C)

Behaviour (in water): reacts and sinks, hydrolyzes to acetic acid, liberating heat
Behaviour (in air): vapours are heavier than air, react with moisture to produce acetic acid
Odour Threshold Range: 0.14-0.36 ppm

ENVIRONMENTAL CONCERNS

Acetic anhydride hydrolyzes to acetic acid, which is harmful to aquatic life in low concentrations. Acetic anhydride and acetic acid show no potential for biological accumulation or food chain contamination.

HUMAN HEALTH

TLV®: 5 ppm (20 mg/m^3)
IDLH: 1000 ppm

Exposure Effects

Inhalation: Inhalation will cause irritation to mucous membranes and respiratory tract. Vapours can cause burns, coughing, chest pain, nausea, and vomiting

Contact: Contact with the eyes will cause serious eye burns, vision impairment, possible photophobia, lacrimation and corneal edema. Contact with the skin will cause burns, wrinkling and whitening of skin, allergic sensitization, and eventually dermatitis

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE AND COMBUSTIBLE". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and inhalation of vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Use foam, dry chemical, or carbon dioxide to extinguish. Water should only be used if absolutely necessary. Cool fire-exposed containers with water. Avoid getting water inside containers.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb residual liquid with sorbents. Neutralize contaminated area with lime and shovel into containers for disposal

Water: Contain by damming, water diversion or natural barriers. Neutralize with lime or sodium bicarbonate. If possible, remove water for treatment

Air: Use water spray to knock down and disperse vapour. Control runoff for later treatment and/or disposal

NAS HAZARD RATING

Category	Rating
Fire	2
Health	
Vapour Irritant	3
Liquid or Solid Irritant	3
Poison	3
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	2
Aesthetic Effect	2
Reactivity	
Other Chemicals	3
Water	2
Self-reaction	0

NFPA
HAZARD
CLASSIFICATION

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Clear, colourless liquid (Celanese PB 1978)
Usual shipping state	Liquid
Physical state at 15°C, 1 atm	Liquid
Melting point	-73.13°C (Kirk-Othmer 1978)
Boiling point	139.55°C (CRC 1980; Ullmann 1975) 138.63°C (Kirk-Othmer 1978)
Vapour Pressure	0.4 kPa (20°C) (Ullmann 1975)

Densities

Density	1.0820 g/mL (20°C) (Kirk-Othmer 1978)
Specific gravity of liquid (water = 1)	1.082 (20°/4°C) (CRC 1980)
Specific gravity of vapour (air = 1)	3.52 (Verschueren 1984)

Fire Properties

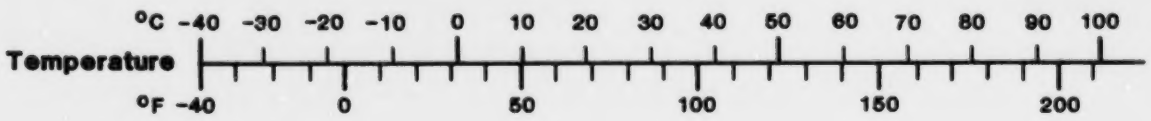
Flammability	Combustible liquid (NFPA 1978)
Flash point CC OC	49°C (NFPA 1978) 64°C (Celanese MSDS 1979)
Autoignition temperature	316°C (NFPA 1978)
Burning rate	3.3 mm/min (CHRIS 1978)
Upper flammability limit	10.3 percent (v/v) (NFPA 1978)
Lower flammability limit	2.9 percent (v/v) (NFPA 1978) 2 percent (v/v) (Ullmann 1975)
Heat of combustion	1806 kJ/mole (25°C) (CRC 1980)
Combustion products	Carbon dioxide and water (CRC 1980)
Decomposition temperature	280°C (Kirk-Othmer 1978)
Decomposition product	Ketene (Kirk-Othmer 1978)
Explosiveness	Vapours form explosive mixtures with air (NFPA 1978)

Other Properties

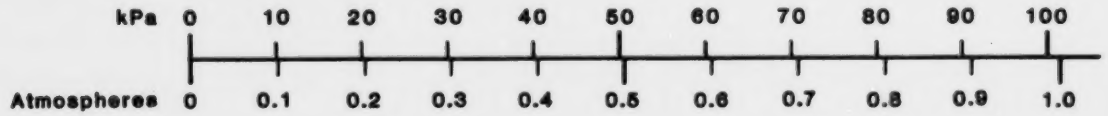
Molecular weight of pure substance	102.09 (CRC 1980)
Constituent components of typical commercial grade	Pure: Acetic Anhydride 99.0 percent minimum Technical: 78-98.5 percent acetic anhydride

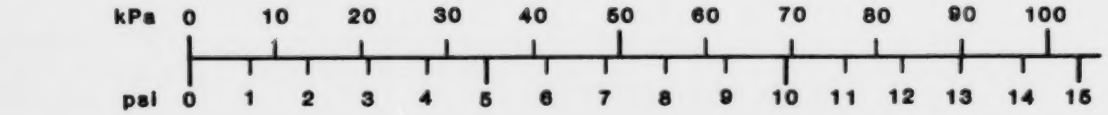
	Remainder: water and some acetic acid (Celanese PB 1978)
Refractive index	1.39006 (20°C) (CRC 1980)
Viscosity	0.90/mPa·s (20°C) (Kirk-Othmer 1978)
Liquid interfacial tension with air	32.7 mN/m (20°C) (CRC 1980)
Latent heat of fusion	10.5 kJ/mole (at melting point) (Lange's Handbook 1979)
Latent heat of sublimation	48.3 kJ/mole (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	45.7 kJ/mole (at boiling point) (CRC 1980)
Heat of formation	-619.1 kJ/mole (25°C) (Sussex 1977)
Heat capacity	
constant pressure (C_p)	185.5 J/(mole·°C) (20°C) (Kirk-Othmer 1978)
constant volume (C_v)	172 J/(mole·°C) (25°C) (CHRIS 1978)
Critical pressure	4680 kPa (Ullmann 1975)
Critical temperature	296°C (Ullmann 1975)
Coefficient of thermal expansion	1.13×10^{-9}/°C (18°C) (Ullmann 1975)
Thermal conductivity	0.136 W/(m·K) (30°C) (Kirk-Othmer 1978)
Saturation concentration	19 g/m^3 (20°C), 38 g/m^3 (30°C) (Verschueren 1984)
Dielectric constant	22.1 (Kirk-Othmer 1978)
Dipole moment	9.3×10^{-30} C·m (Kirk-Othmer 1978)
Specific conductivity	2.3×10^{-8} ohm^{-1} cm^{-1} (Kirk-Othmer 1978)
Evaporation rate	0.12 g/(m^2·s) (20°C, wind 4.5 m/s) (this work)
Solubility	
In water	Slightly soluble. (Nominally 12 percent by weight at 20°C.) Reacts to form acetic acid (Celanese PB 1978)
In other common materials	Miscible in ethanol, carbon tetrachloride, and diethyl ether. Soluble in chloroform (Celanese PB 1978)
Vapour Weight to Volume Conversion Factor	1 ppm = 4.240 mg/m^3 (20°C) (Verschueren 1984)

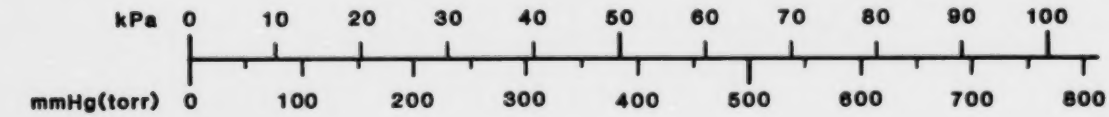
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







Viscosity

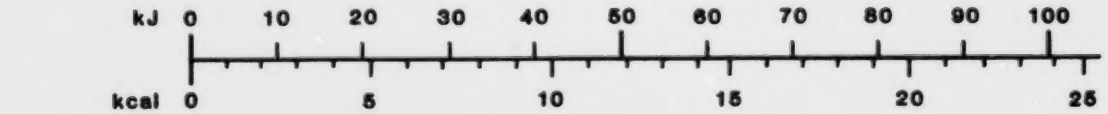
Dynamic 1 Pa·s = 1 000 centipoise (cP)

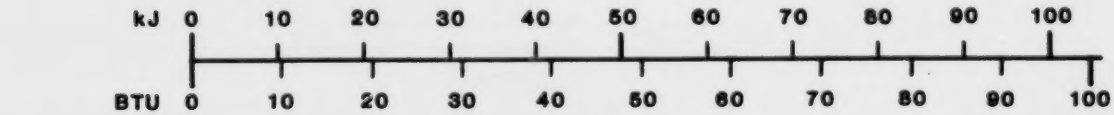
Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J





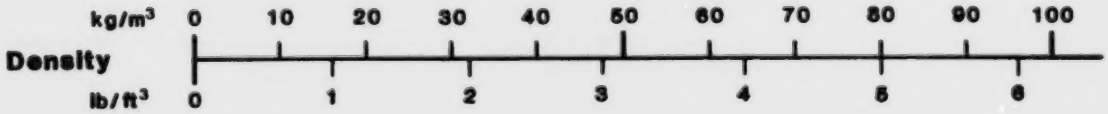


FIGURE 1

ACETIC ANHYDRIDE

VAPOUR PRESSURE VS TEMPERATURE

Reference: ULLMANN 1975

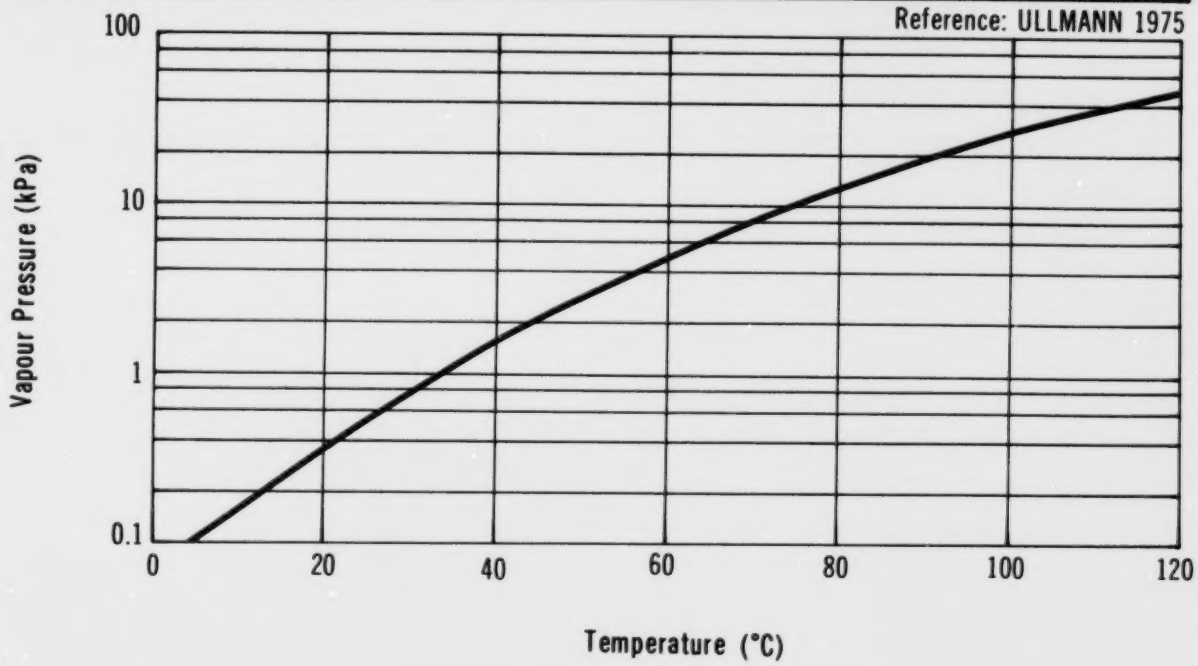


FIGURE 2

ACETIC ANHYDRIDE

LIQUID VISCOSITY

Reference: ULLMANN 1975

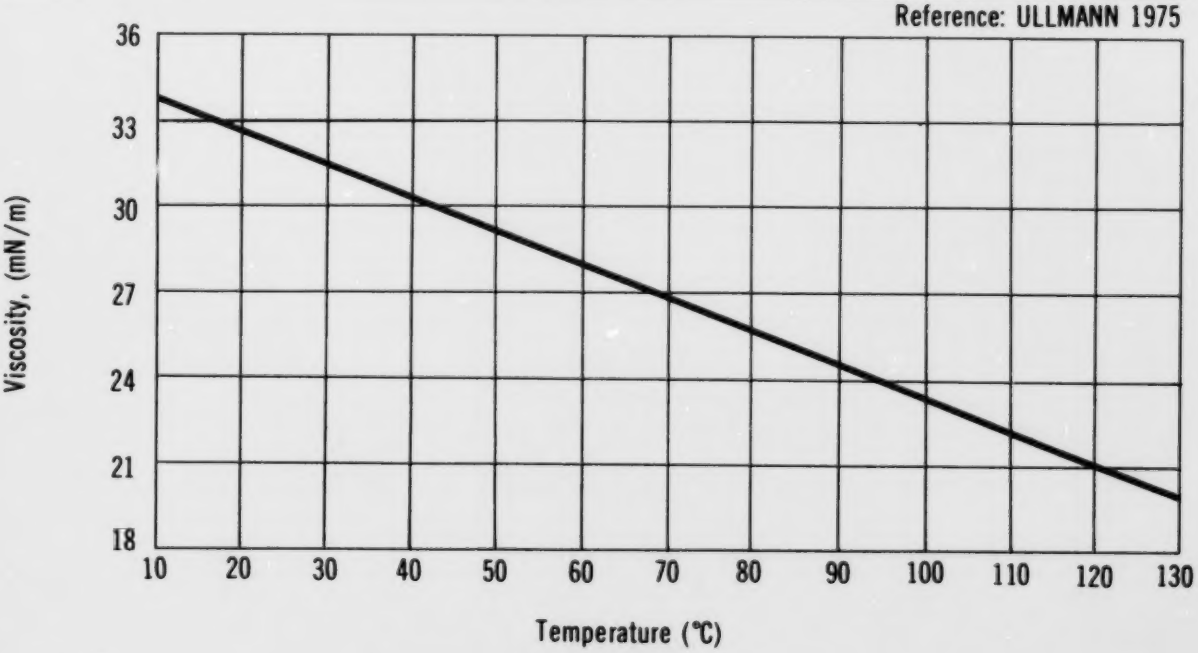


FIGURE 3

ACETIC ANHYDRIDE

LIQUID DENSITY vs TEMPERATURE

Reference: CHRIS 1978

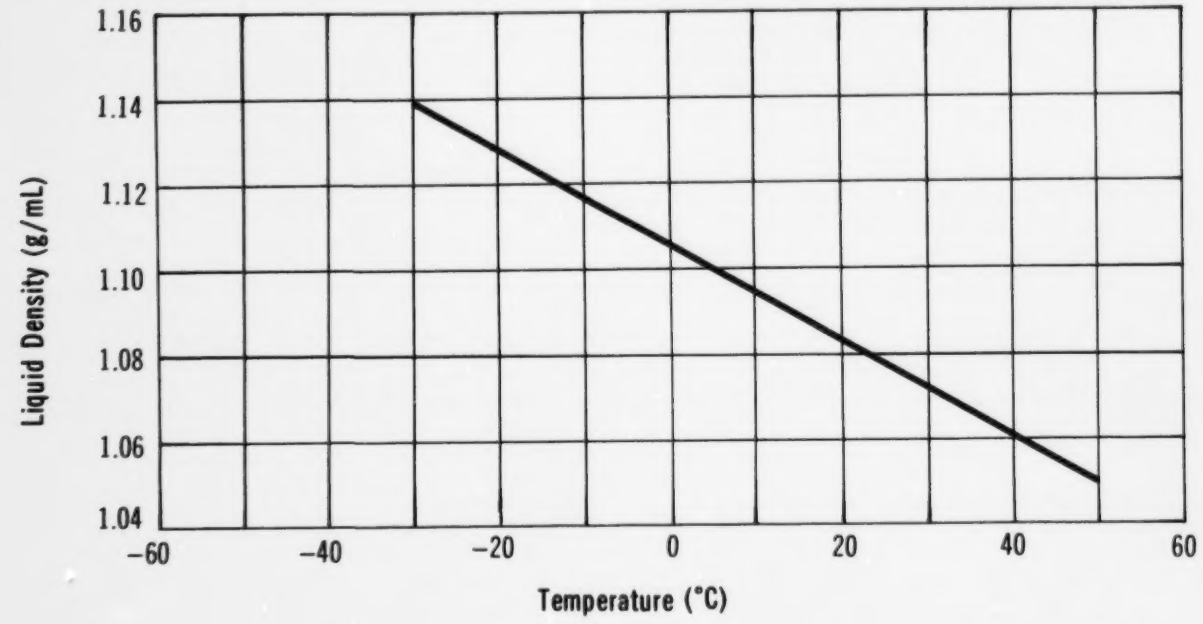
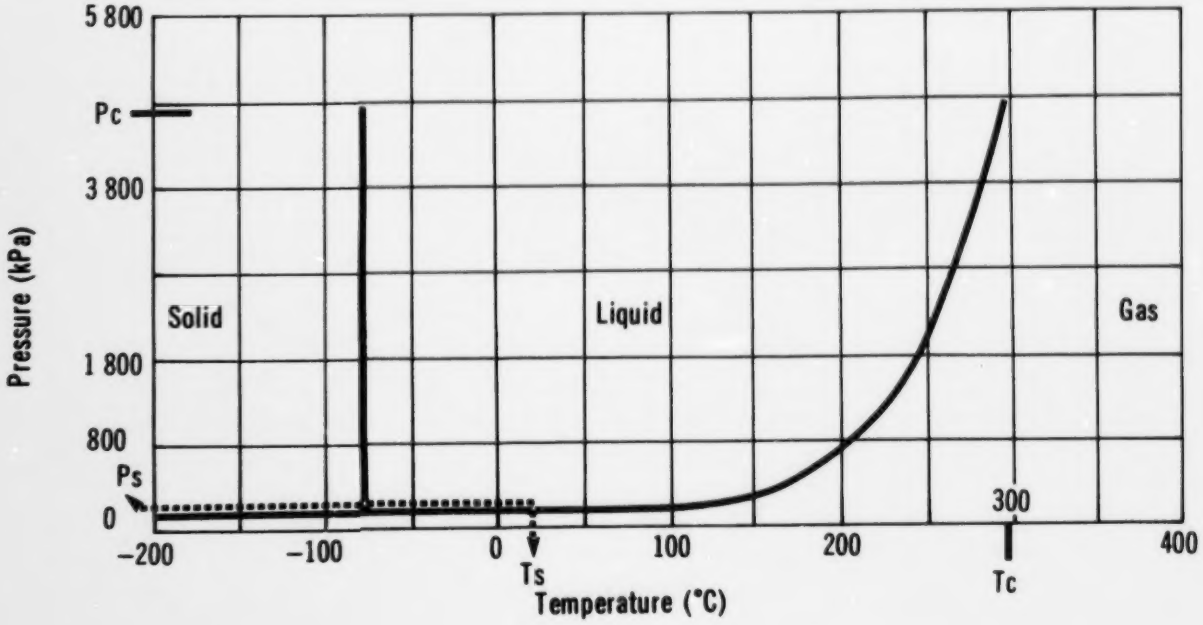


FIGURE 4

ACETIC ANHYDRIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Celanese PB 1978)

Acetic anhydride is available in a pure form with a minimum purity of 99.0 percent. It is also available in a technical grade with minimum purities of 78, 85, 90-95, 97.5, and 98.5 percent.

3.2 Domestic Manufacturer (CCPA 1981; CBG 1980)

Celanese Canada Inc.
800 Dorchester Blvd. West
Montreal, Quebec
H3C 3K8
(514) 878-1581

3.3 Other Suppliers (CBG 1980)

A & K Petro-Chem Industries Ltd.
710 Arrow Road
Weston, Ontario
M9M 2M1
(416) 746-2991

Cote Chemicals Inc.
111 Bombardier Park
Chateauguay Centre, Quebec
J6J 3X0
(514) 691-6260

Harrisons & Crosfield (Canada) Ltd.
4 Banigan Drive
Toronto, Ontario
M4H 1G1
(416) 425-6500

Henley Chemicals Ltd.
1735 Bayly Street
Pickering, Ontario
L1W 3G7
(416) 831-3341

Stanchem Div PPG Ind. Canada Ltd.
5029 St. Ambroise Street
Montreal, Quebec
H4C 2E9
(514) 933-6721

Van Waters & Rogers Ltd.
9800 Van Horne Way
Richmond, British Columbia
V6X 1W5
(604) 273-1441

Winfield Chemical Industries Ltd.
P.O. Box 1134
Woodstock, New Brunswick
E0J 2B0
(506) 328-6851

3.4 Major Transportation Routes

Current Canadian production of acetic anhydride is in Edmonton, Alberta. The product is shipped to Ontario, Quebec, British Columbia and New Brunswick.

3.5 Production Levels (PC Celanese 1982)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Celanese Canada, Edmonton, Alberta	35 000 (about half is for captive use)

3.6 Manufacture of Acetic Anhydride (FKC 1975; Kirk-Othmer 1978)

3.6.1 General. Acetic acid (glacial) is dehydrated catalytically to form ketene, which in turn reacts with acetic acid to form the anhydride.

3.6.2 Manufacturing Process. Glacial acetic acid vapour is passed through a tubular reactor with a small amount of catalyst (triethyl phosphate) at 700-800°C and 10-27 kPa:

$$CH_3CO_2H \longrightarrow CH_2=C=O + H_2O$$
$$CH_2=C=O + CH_3CO_2H \longrightarrow (CH_3CO)_2O$$

As the reactants leave the reactor, the dehydration catalyst is neutralized (with ammonia) to prevent reversion of the reaction. The reaction product passes through a series of condensers to separate the ketene and acetic anhydride from water and unreacted acetic acid. Final purification is by fractional distillation. Overall yield is about 85-90 percent.

3.7 Major Uses in Canada (Celanese PB 1978)

Acetic anhydride is used in the acetylation of cellulose to produce acetate fibres, plastics, coatings and films; for the direct esterification of alcohols; in the manufacture of drugs, pharmaceuticals and intermediate explosives; in herbicides; and in paper and textiles treatment.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

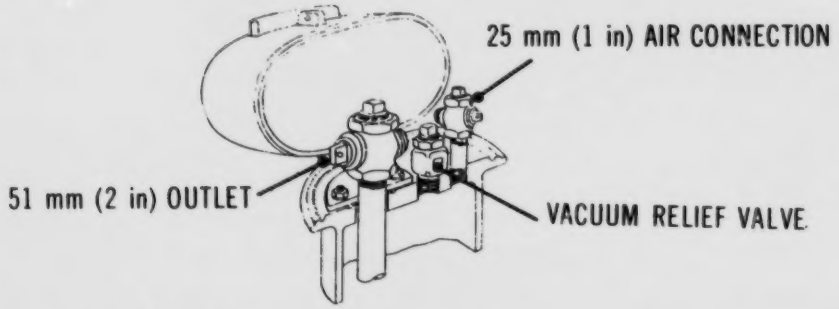
4.1.1 Bulk Shipment. Acetic anhydride solutions are shipped bulk in specially designed railway tank cars and tank motor vehicles.

4.1.1.1 Railway tank cars. Railway tank cars used in the transportation of acetic anhydride are listed in Table 2 (RTDCR 1974; TCM 1979). Figure 5 shows a 111A60W1 railway car. Table 3 indicates railway tank car details associated with this drawing. Acetic anhydride cars may be unloaded through bottom outlets; an approved pump is preferred for unloading from the top (MCA 1962). The liquid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with a 51 mm (2 in.) unloading connection valve.

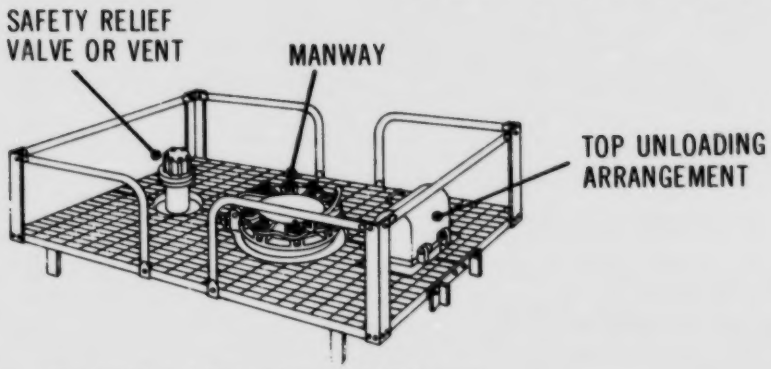
4.1.1.2 Tank motor vehicles. The capacity of tank trucks transporting acetic anhydride is usually about 18 200 kg (40 000 lb.) minimum (Celanese MSDS 1978).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
111A60W1 (1L)	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Safety vent 414 kPa (60 psi) or safety valve 242 kPa (35 psi). Interior coated. Test pressure 414 kPa (60 psi).
111A60ALW1	Aluminum fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Safety vent 414 kPa (60 psi) or safety valve 242 kPa (35 psi). Bottom outlet or washout optional. Test pressure 414 kPa (60 psi).



Detail of top unloading arrangement



Detail of loading platform

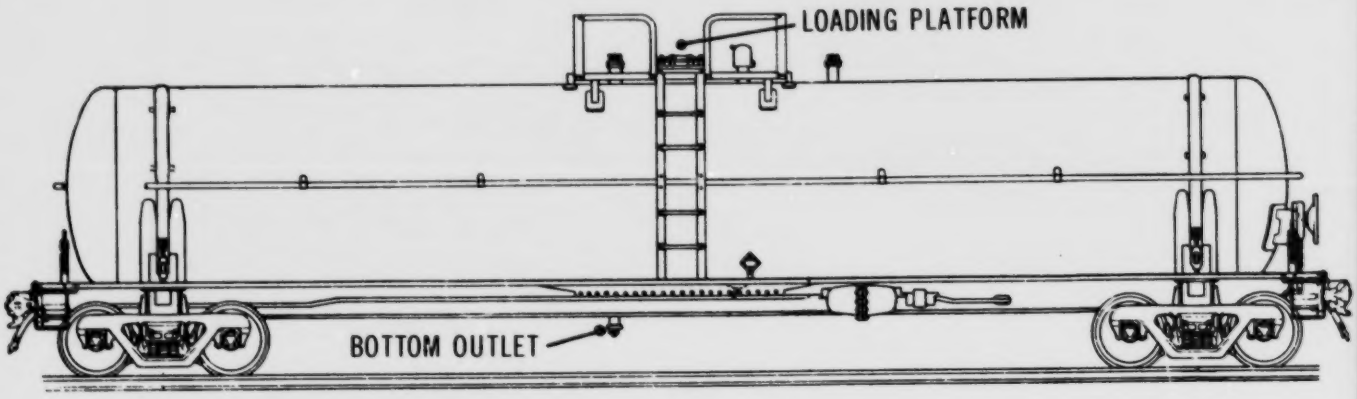


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATION - CLASS 111A60W1

Description	Tank Car Size (Imp. Gal.) 16 700	17 200	20 000
Overall			
Nominal capacity	75 700 L (16 700 gal.)	78 000 L (17 200 gal.)	90 900 L (20 000 gal.)
Car weight - empty	33 900 kg (74 700 lb.)	33 900 kg (74 700 lb.)	38 900 kg (85 800 lb.)
Car weight - (max.)	119 000 kg (263 000 lb.)	83 500 kg (184 000 lb.)	119 000 kg (263 000 lb.)
Tank			
Material	Steel	Steel	Steel
Thickness	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)
Inside diameter	2.60 m (102 in.)	2.62 m (103 in.)	2.74 m (108 in.)
Test pressure	414 kPa (60 psi)	414 kPa (60 psi)	414 kPa (60 psi)
Burst pressure	1640 kPa (240 psi)	1640 kPa (240 psi)	1640 kPa (240 psi)
Approximate Dimensions			
Coupled length	17 m (57 ft.)	17 m (57 ft.)	18 m (60 ft.)
Length over strikers	16 m (53 ft.)	16 m (53 ft.)	17 m (57 ft.)
Length of truck centres	13 m (42 ft.)	13 m (42 ft.)	14 m (45 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)	4 m (13 ft.)
Overall height	5 m (15 ft.)	5 m (15 ft.)	5 m (15 ft.)
Overall width (over grabs)	3.2 m (127 in.)	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2-3 m (8-10 ft.)	2-3 m (8-10 ft.)	2-3 m (8-10 ft.)
Width of grating	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)
Loading/Unloading Fixtures			
Top Unloading			
Unloading connection	51 mm (2 in.)	51 mm (2 in.)	51 mm (2 in.)
Manway/fill hole	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)
Air connection	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)
Bottom Unloading			
Bottom oulet	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)
Safety Devices	Safety vent or valve		
Dome	None		
Insulation	Optional		

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (Cont'd)

CTC/DOT* Specification Number	Description
103ALW	Aluminum fusion-welded tank with dome. Uninsulated or insulated. 2% dome. Safety valves 242 kPa (35 psi) or safety vent 414 kPa (60 psi). Bottom outlet or washout optional. Test pressure 414 kPa (60 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

Similar to railway tank cars, these highway tankers are unloaded from the top, usually the stand pipe being extended down over the back of the tank. A pump is used for unloading; air pressure should not be used (MCA 1962).

Tank motor vehicles are not specifically regulated under Transport Canada Specifications. Acetic anhydride solutions are not transported under pressure.

4.1.2 Packaging. In addition to bulk shipments, acetic anhydride is also transported in drums. Drums fabricated from a variety of construction materials are permitted. Table 4 listing drum types and descriptions is included (TDGC 1980).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1962):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.

Proceed with off-loading as follows (MCA 1962):

- Ensure that tank car is electrically bonded to the ground.
- Relieve tank car of all internal pressure.
- Connect the 51 mm (2 in.) unloading line to the discharge outlet at the top of the tank.

- Commence unloading by pumping.
- Reverse the above procedure to close up the car.

TABLE 4 DRUMS

Type of Drum	Designation	Description	Figure No. (If Any)
Steel	1A1	Nonremovable head, reusable	6
	1A1A	1A1 with reinforced chime	6
	1A1B	1A1 with welded closure flange	6
	1A1C	1A1 with lead coating	6
	1A1D	1A1 with coating (other than lead)	6
	1A3	Nonremovable head, single use only	6
Plastic	1H1	Nonremovable head. Maximum capacity 250 L (55 gal.) Maximum net mass 400 kg (882 lb.)	
Steel Drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.)	
Monel*	TC5M		6
Nickel	TC5K	Similar to monel drum, only nickel	

* See Section 4.3

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles. The unloading of tank trailers is similar to that of railway tank cars. The general procedures for tank cars apply equally well to tank trailers.

4.2.3 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used. It is recognized that other materials may be used for particular applications, as indicated in Table 5.

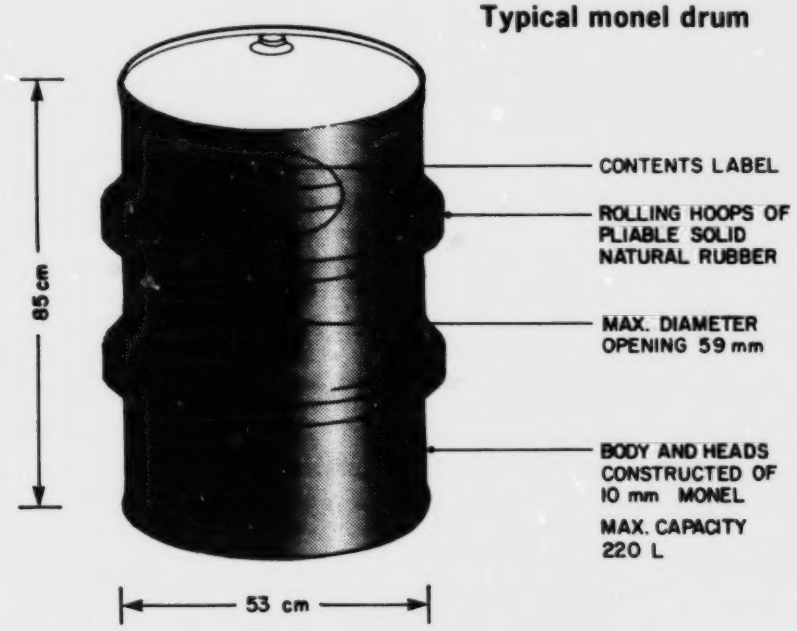
Schedule 40 stainless steel 316 pipes and welding fittings are recommended (MCA 1962). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak.

FIGURE 6

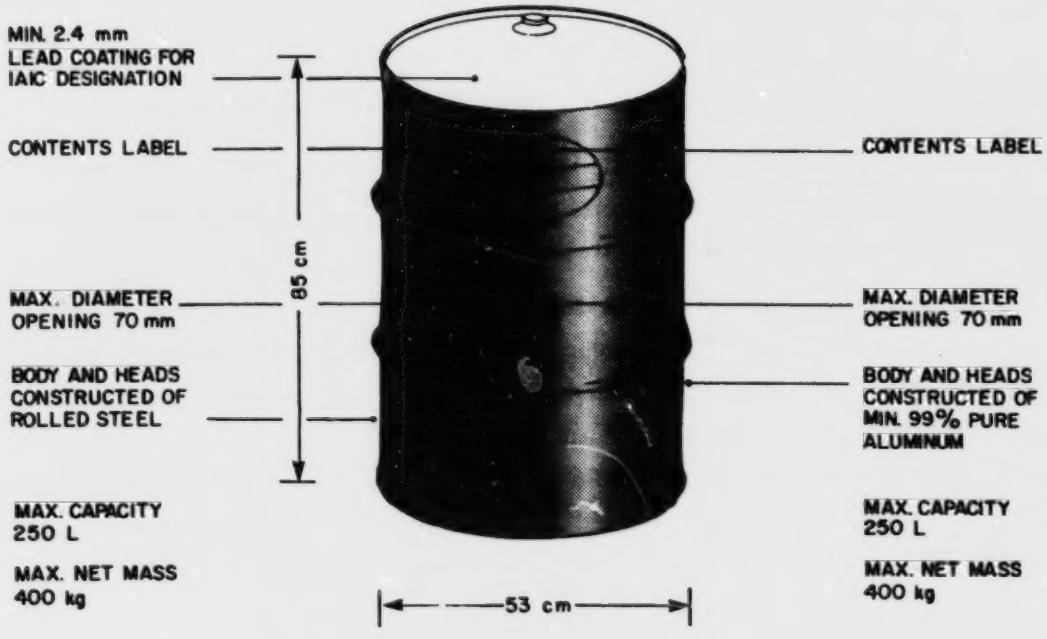
ACETIC ANHYDRIDE

TYPICAL DRUM CONTAINERS

Typical monel drum


85 cm
53 cm
CONTENTS LABEL
ROLLING HOOPS OF PLIABLE SOLID NATURAL RUBBER
MAX. DIAMETER OPENING 59 mm
BODY AND HEADS CONSTRUCTED OF 10 mm MONEL
MAX. CAPACITY 220 L

Typical steel drum


MIN. 2.4 mm LEAD COATING FOR IAIC DESIGNATION
CONTENTS LABEL
MAX. DIAMETER OPENING 70 mm
BODY AND HEADS CONSTRUCTED OF ROLLED STEEL
MAX. CAPACITY 250 L
MAX. NET MASS 400 kg
85 cm
53 cm
CONTENTS LABEL
MAX. DIAMETER OPENING 70 mm
BODY AND HEADS CONSTRUCTED OF MIN. 99% PURE ALUMINUM
MAX. CAPACITY 250 L
MAX. NET MASS 400 kg

The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on tank cars; however, process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Steel or stainless steel pipes and swivel joints may be used for flexible sections at rail car unloading stations. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance.

For valving, cast steel or cast iron diaphragm valves lined with polyvinylidene fluoride will serve adequately (DPLV 1972). Refer to Table 5 for other material possibilities.

A single-suction centrifugal pump with "20" alloy shaft and impeller and a high silicon cast iron casing is recommended for pumping. Teflon is a good packing material (HIS 1969).

Welded stainless steel storage tanks or polypropylene lined carbon steel tanks are commonly used.

4.3 Compatibility with Materials of Construction

The compatibility of acetic anhydride with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings					PVC I PE (MWPP 1978)
	All	23			PVC I PVC II (DPPED 1967)

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (Cont'd)		24	PVDF, PP PVDC (DCRG 1978)		
		66	Chlorinated Polyether (DCRG 1978)		
2. Valves		Boiling	SS J-20 SS 316 (JSSV 1979)		
3. Pumps	100%	To boiling	SS 304 SS 316 High Silicon Cast Iron (HIS 1969)		GRP
4. Storage	All	To boiling	Aluminum SS CS Resin-lined (MCA 1962)	Copper	CS, CI (MCA 1962)
5. Others	60%	85	SS 302 SS 304 SS 316 (ASS)		
	90%	20	SS 302 SS 304 SS 316 (ASS)	SS 430 (ASS)	
	Technically Pure	20	PP (GF)	PE (GF)	uPVC, POM. NR, NBR, IIR, EPDM CR, FPM CSM (GF)
	Technically Pure	80			PP, PE uPVC, NR POM, NBR IIR, EPDM CR, FPM CSM (GF)

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	-	21	PVDF (TPS 1978)		
	-	22			PVC CPVC (TPS 1978)
		66			PVDF (TPS 1978) SBR (GPP)
	To 100%	24 to 100	Glass (CDS 1967)		
	50%	24 to 149	Glass (CDS 1967)		
	100%	24			Concrete Wood (CDS 1967)
	Most	Most			Iron or Steel (Ullmann 1975)

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Aluminum
CI	Cast Iron, Austenitic
	Cast Iron, High Silicon
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Copper
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)

TABLE 6 MATERIALS OF CONSTRUCTION (Cont'd)

Abbreviation	Material of Construction
	Glass
GPR	Glass Reinforced Vinyl Ester
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
	Polytetrafluoroethylene (Teflon)
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (Followed by grade)	Stainless Steel
	"20" Alloy (Durimet 20, Carpenter 20)
uPVC	Unplasticized Polyvinyl Chloride
	Wood

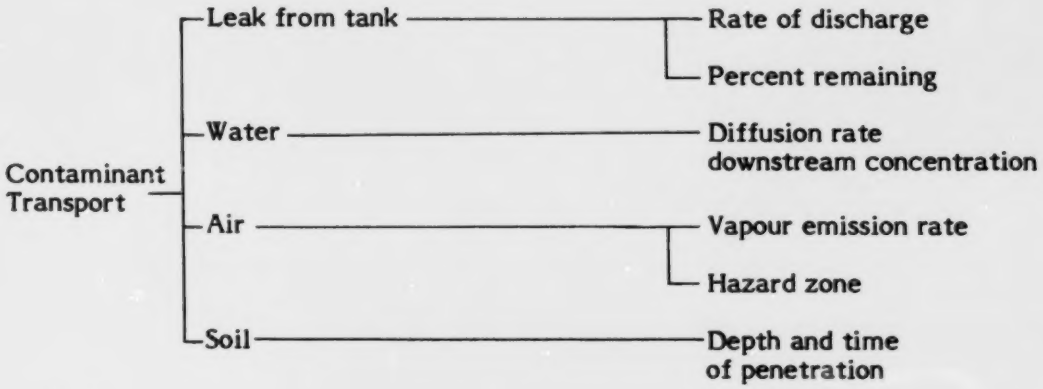
5 CONTAMINANT TRANSPORT

5.1 General Summary

Acetic anhydride is transported in liquid form. When spilled in water, acetic anhydride will sink and react slowly, producing acetic acid and liberating heat. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may be an environmental concern.

Acetic anhydride has a relatively low volatility; the vapour released from a liquid pool on the ground surface may be sufficient to be of concern.

The following factors are considered for the transport of a spill in water and soil:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Acetic anhydride is commonly transported in specially designed railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with acetic anhydride is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of acetic anhydride and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

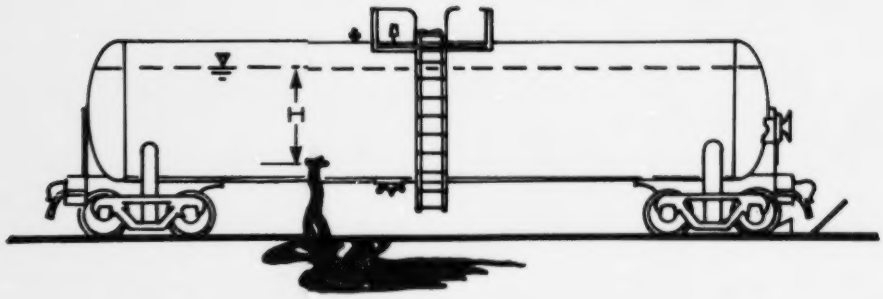


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a vent hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the liquid above the puncture hole (H), and a coefficient of discharge (Cd).

5.2.2 Nomograms.

5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of acetic anhydride. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

FIGURE 8

ACETIC ANHYDRIDE

PERCENT REMAINING VS TIME

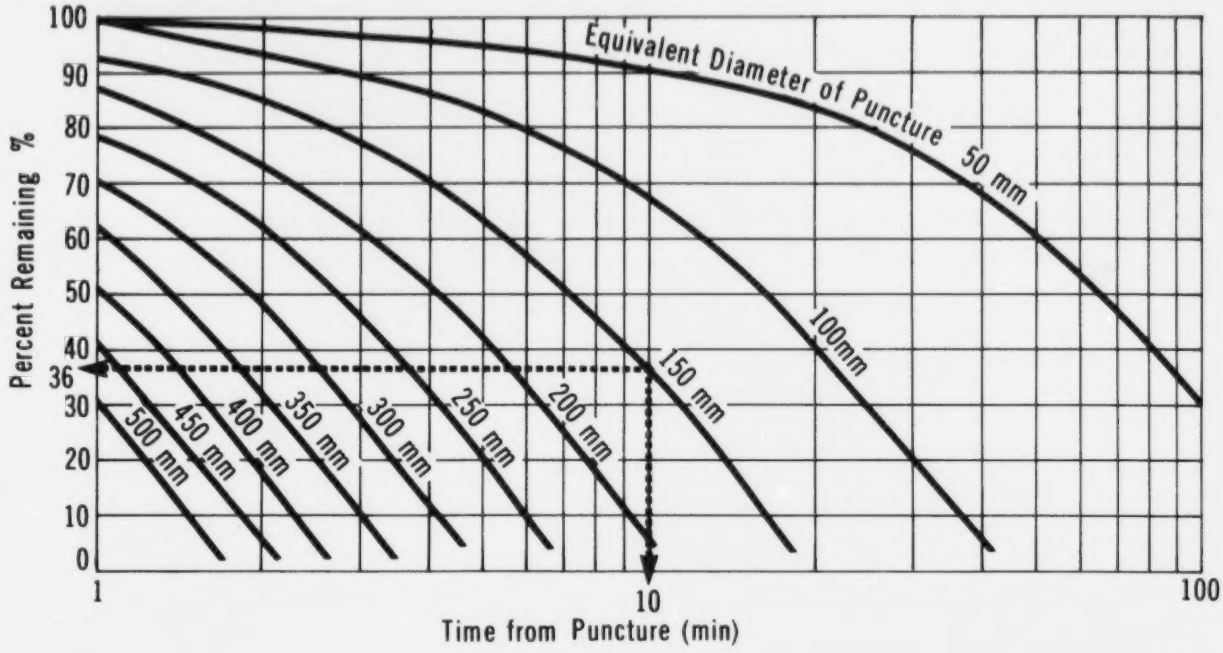
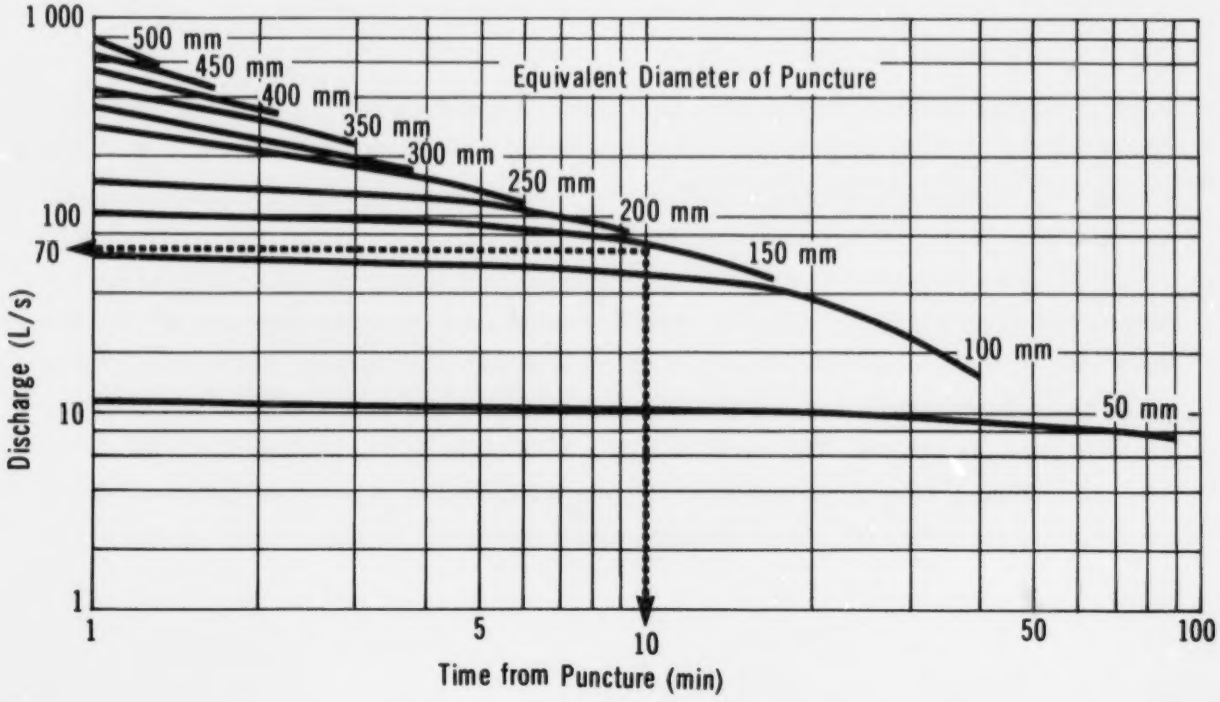


FIGURE 9

ACETIC ANHYDRIDE

DISCHARGE RATE VS TIME



5.2.2.2 Figure 9: Discharge rate versus time. Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car (2.75 Ø x 13.4 m long) filled with acetic anhydride has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 8
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as in Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 9
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since acetic anhydride is a liquid with a relatively low volatility, direct venting of the vapour to the atmosphere from a hole in a ruptured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

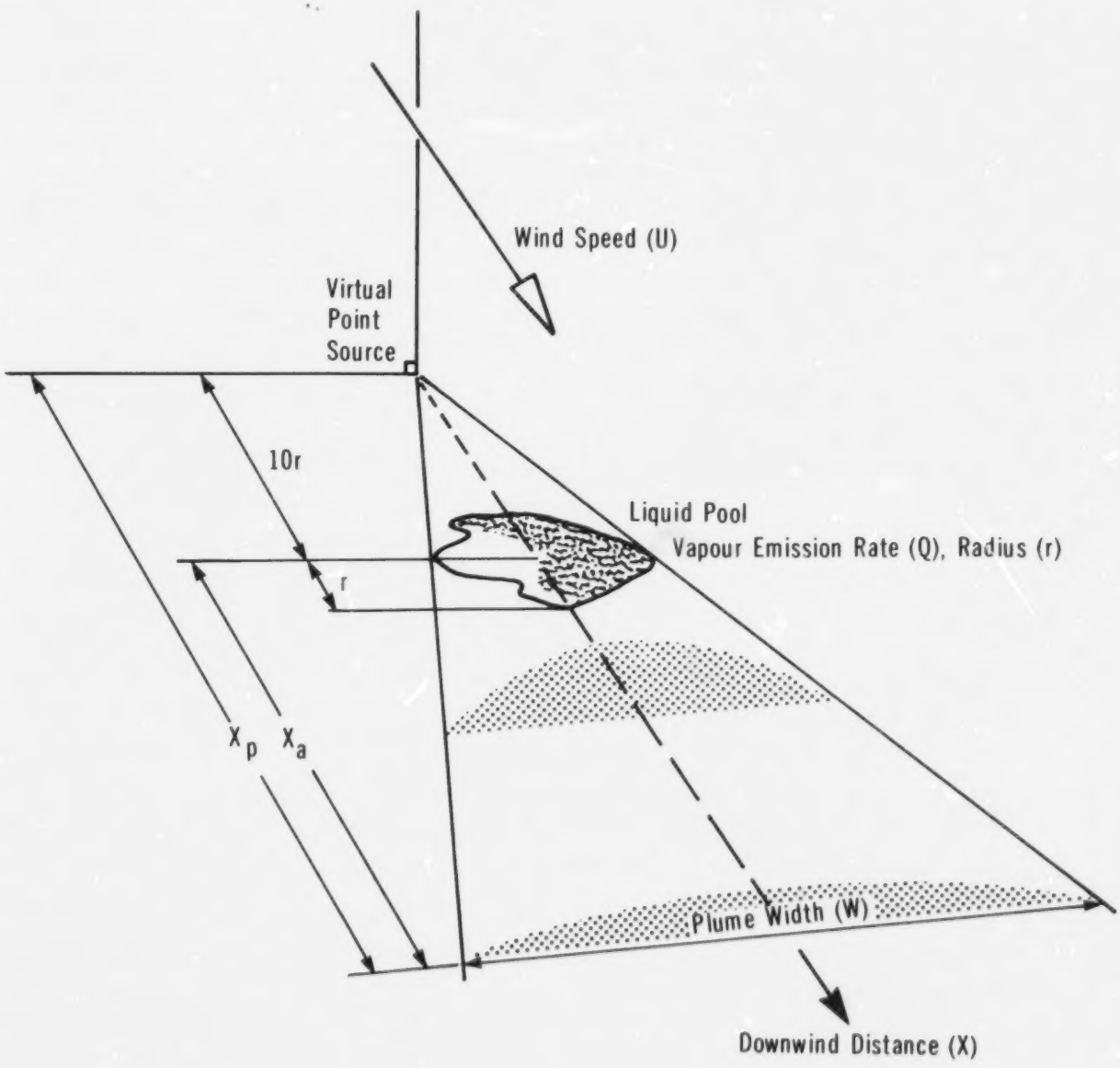
To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 10 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as

FIGURE 10

ACETIC ANHYDRIDE

SCHEMATIC OF CONTAMINANT PLUME



a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in order given):

Figure 12:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 7:	weather conditions
Figure 13:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 8:	maximum plume hazard half-widths
Figure 16:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 11 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 12: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for acetic anhydride has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for acetic anhydride at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.12 g/(m^{2}s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which, at a given wind speed, is dependent on ambient temperature and the vapour pressure (Perry 1973) of acetic anhydride at that temperature. For example, evaporation rates of 0.034 g/(m^{2}s) at 0°C and 0.24 g/(m^{2}s) at 30°C were calculated for a wind speed of 4.5 m/s.

Use: For a pool of acetic anhydride of known radius, the rate (Q) at which acetic anhydride vapour is released to the atmosphere at a given temperature can then be estimated from Figure 12. The solid portions of the curves represent spills of 0.3 to 86 tonnes, the latter representing about one standard 80 000 L rail car load of acetic anhydride. It should be noted that Figure 12 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of acetic

FIGURE 11

ACETIC ANHYDRIDE

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE

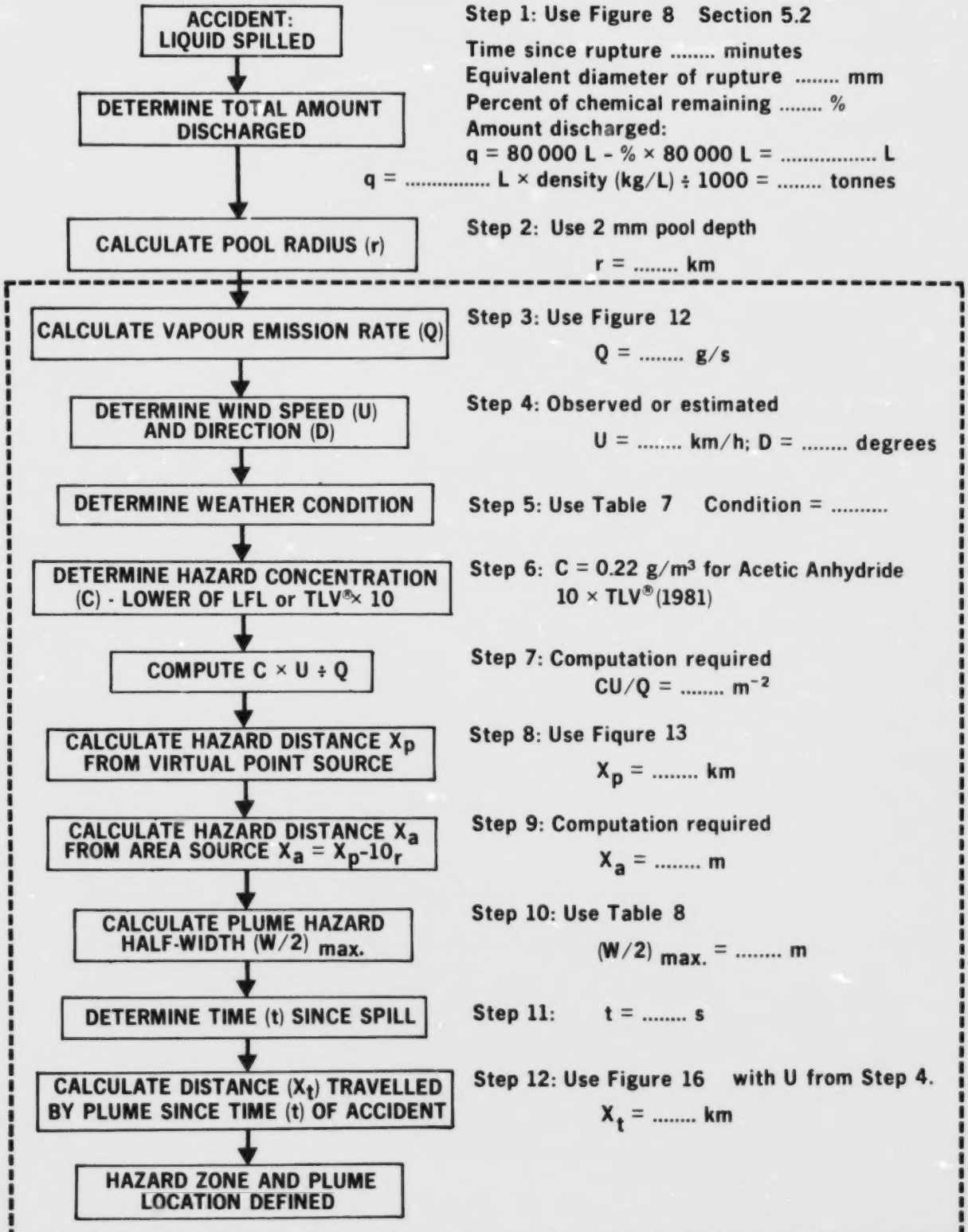
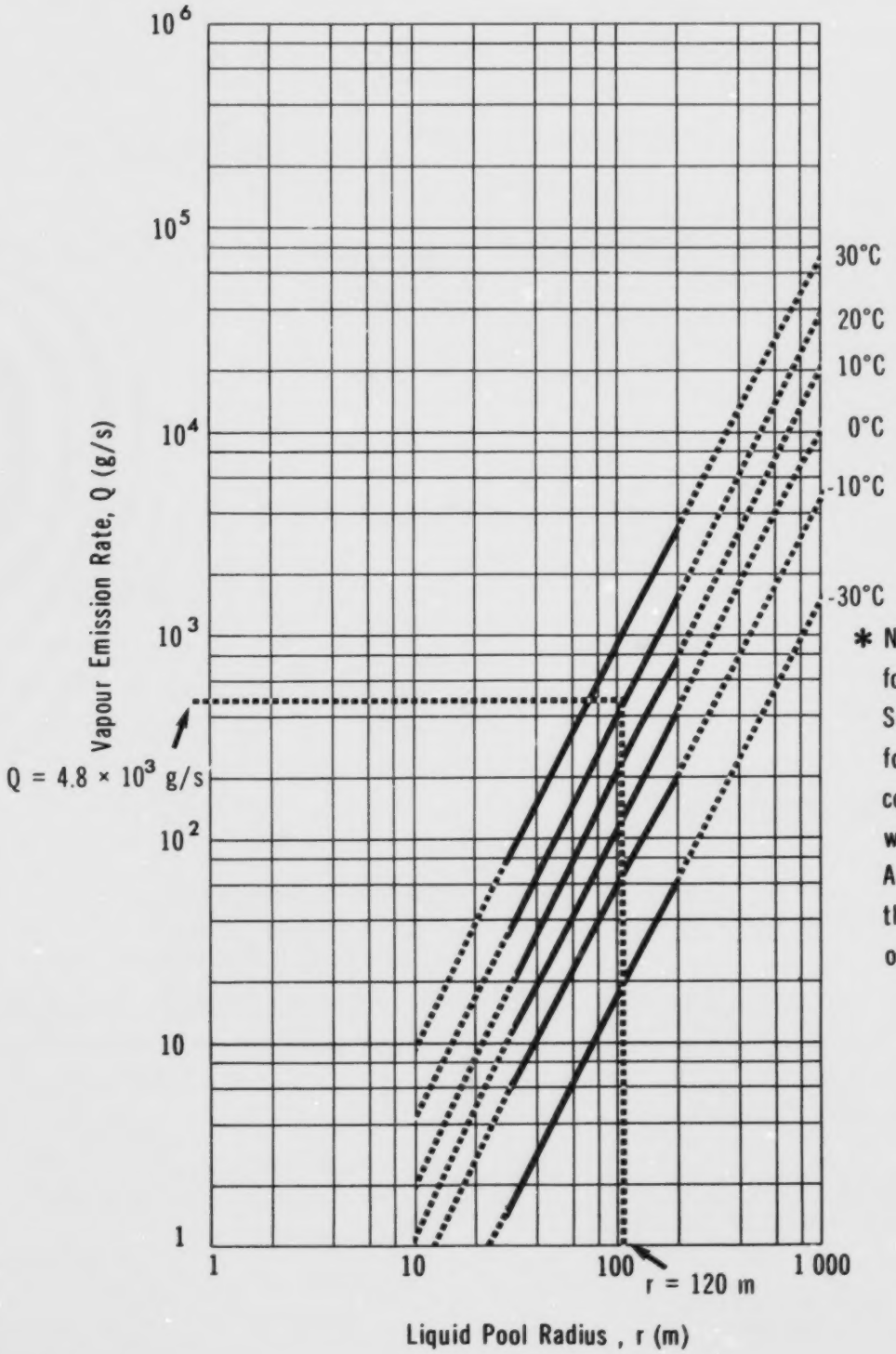

ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
CALCULATE POOL RADIUS (r)
CALCULATE VAPOUR EMISSION RATE (Q)
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV®× 10
COMPUTE C × U ÷ Q
CALCULATE HAZARD DISTANCE Xp FROM VIRTUAL POINT SOURCE
CALCULATE HAZARD DISTANCE Xa FROM AREA SOURCE Xa = Xp-10r
CALCULATE PLUME HAZARD HALF-WIDTH (W/2) max.
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (Xt) TRAVELLED BY PLUME SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PLUME LOCATION DEFINED
Step 1: Use Figure 8 Section 5.2
Time since rupture ..... minutes
Equivalent diameter of rupture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80 000 L - % × 80 000 L = ... L
q = ... L × density (kg/L) ÷ 1000 = ... tonnes
Step 2: Use 2 mm pool depth
r = ... km
Step 3: Use Figure 12
Q = ... g/s
Step 4: Observed or estimated
U = ... km/h; D = ... degrees
Step 5: Use Table 7 Condition = ...
Step 6: C = 0.22 g/m3 for Acetic Anhydride
10 × TLV®(1981)
Step 7: Computation required
CU/Q = ... m-2
Step 8: Use Fiqure 13
Xp = ... km
Step 9: Computation required
Xa = ... m
Step 10: Use Table 8
(W/2) max. = ... m
Step 11: t = ... s
Step 12: Use Figure 16 with U from Step 4.
Xt = ... km

FIGURE 12

ACETIC ANHYDRIDE

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.3 to 86 tonnes.

anhydride vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the emission rate is based on the spill radius on calm water (Table VI, CHRIS 1974). The spill radius employed was arbitrarily chosen as an intermediate value between that of benzene (a moderately volatile liquid) and that of iso-amyl nitrite (a nonvolatile liquid). This model situation was chosen to apply for water-soluble liquids with boiling points above ambient temperature, and to a limited number of water-soluble and water-insoluble organic liquids that are not treated by CHRIS (CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

5.3.2.2 Figure 13: Normalized vapour concentration versus downwind distance. Figure 13 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 13, the weather condition must be determined from Table 7.

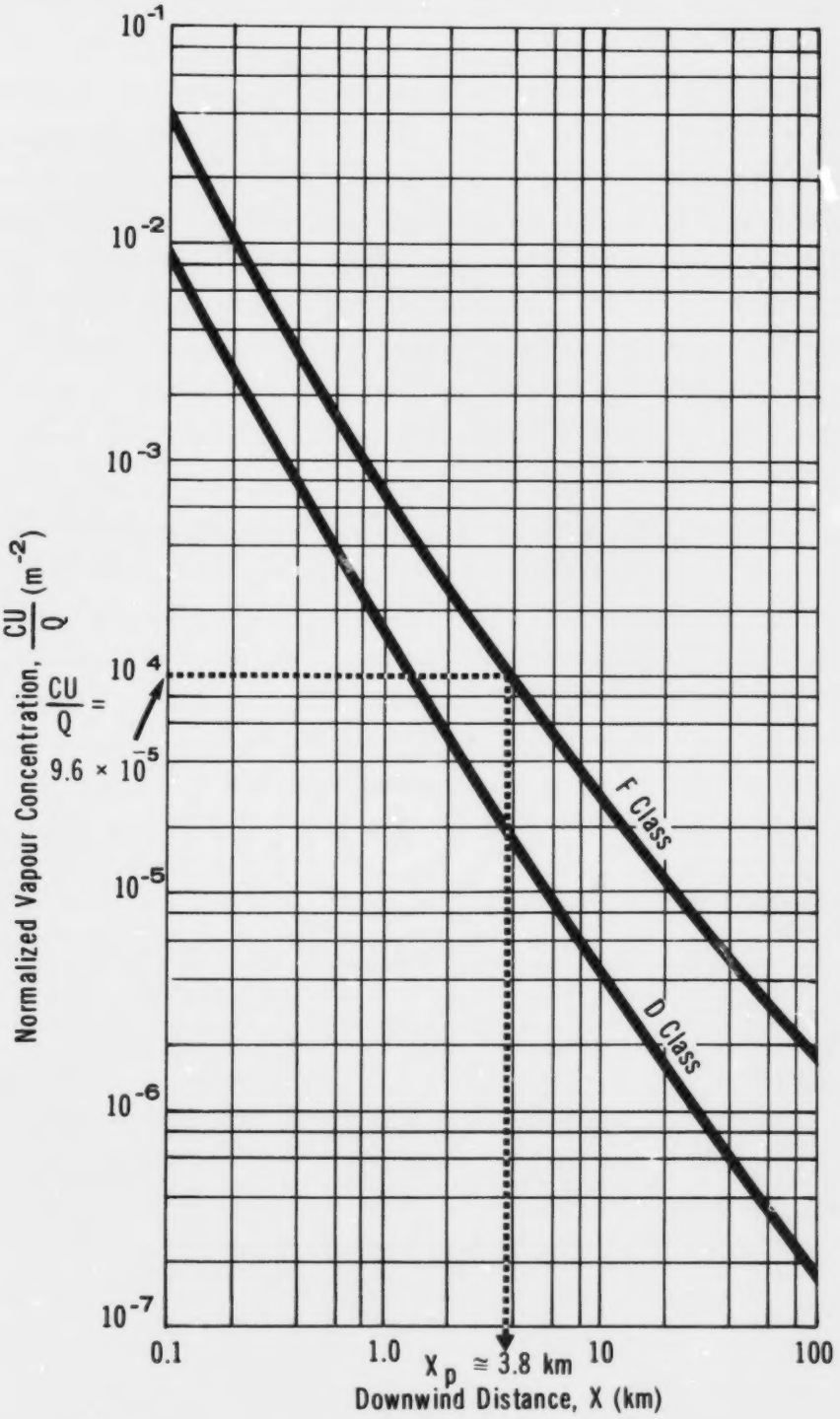
TABLE 7 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed < 11 km/h (~3 m/s) and one of the following:	All other weather conditions
- overcast day	
- night time	
- severe temperature inversion	

FIGURE 13

ACETIC ANHYDRIDE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



Use: The maximum hazard distance, Xp, downwind of the spill can be calculated from Figure 13 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value® (TLV, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV® (in ppm) and the LFL (in percent by volume) to concentrations in g/m^3, use Figures 14 and 15.

A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.3 **Table 8: Maximum plume hazard half-widths.** This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the acetic anhydride Threshold Limit Value (TLV®) of 0.022 g/m^3, or 0.22 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the acetic anhydride vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 8 is therefore only applicable for an acetic anhydride hazard concentration limit of 10 x TLV®, or 0.22 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

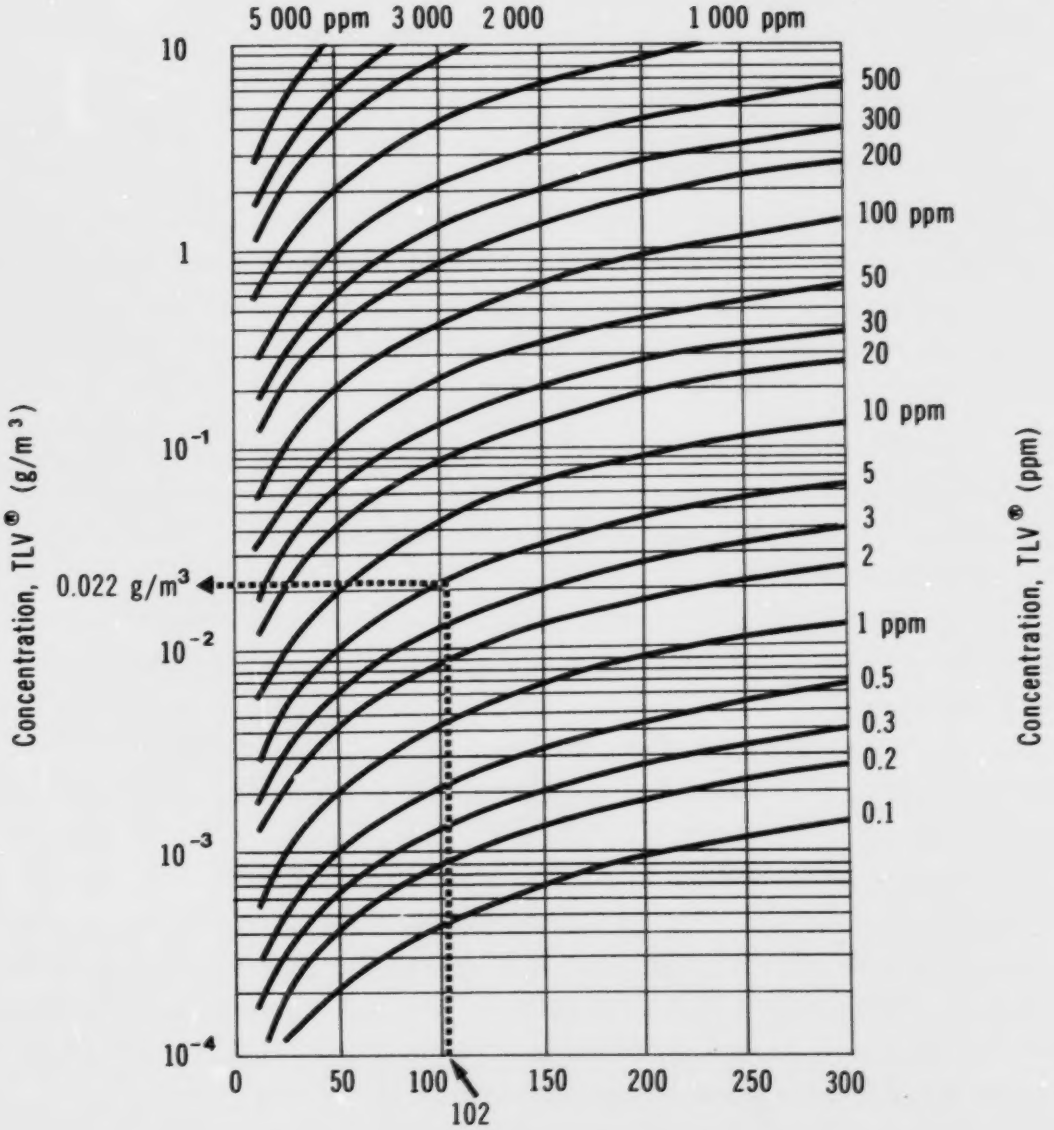
Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used as 7500 to 1 500 000 g/s, corresponding to acetic anhydride spills in the range of about 40 to greater than 8000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 86 400 kg, or approximately 86 tonnes. Therefore, under class D of Table 8, data are provided for up to greater than 90 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 750 to 130 000 g/s, corresponding to acetic anhydride spills in the range of about 1 to 3000 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 34 times a standard rail car load.

FIGURE 14

ACETIC ANHYDRIDE

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



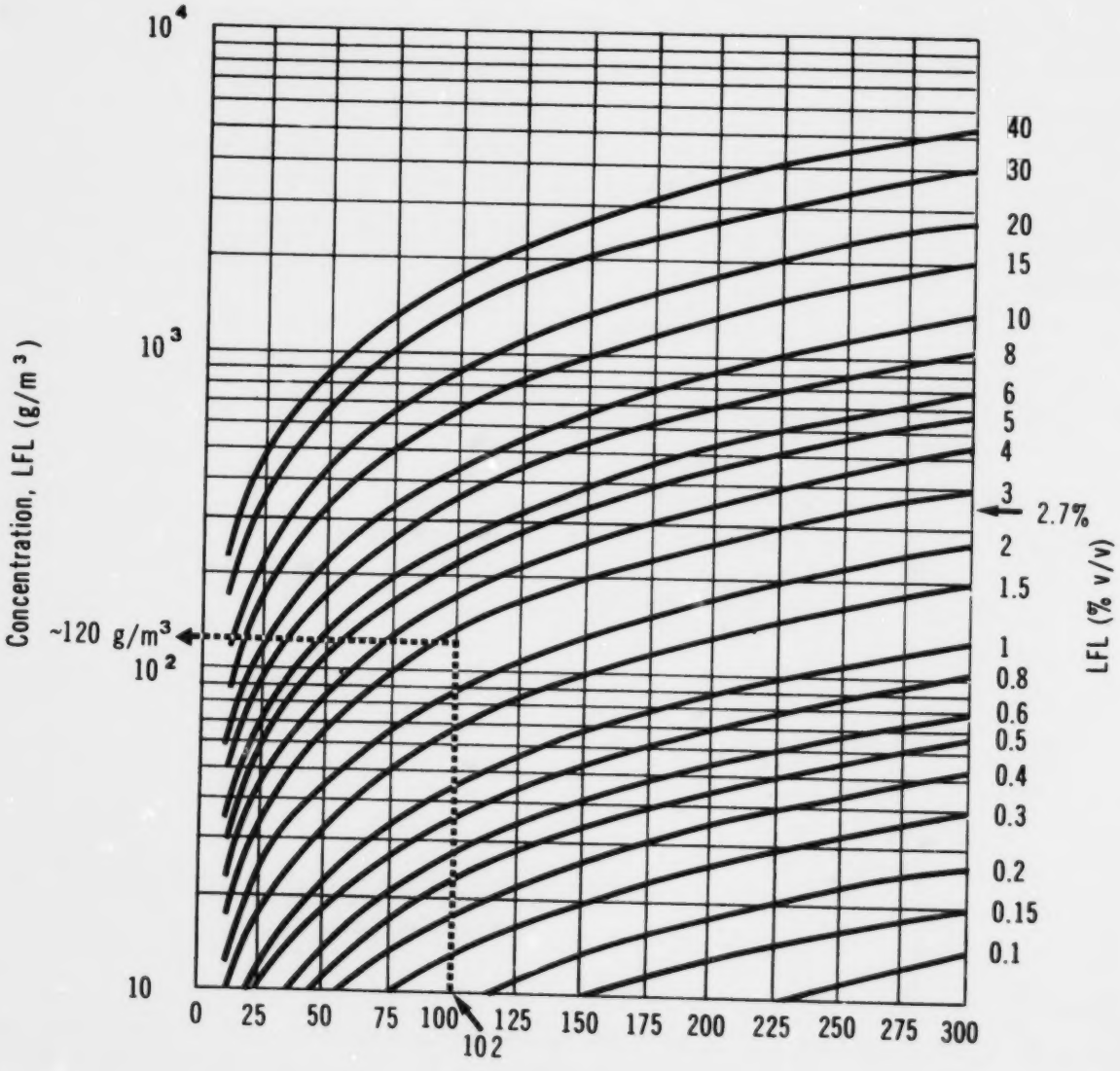
Example: Acetic Anhydride, MW = 102, TLV® = 5 ppm
then TLV® in g/m³ = 0.022

Note: data applicable at 25°C and 760 mm Hg pressure

FIGURE 15

ACETIC ANHYDRIDE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Acetic Anhydride, MW = 102, LFL = 2.7% then LFL in g/m³ = 120

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR ACETIC ANHYDRIDE AT 20°C)

Weather Condition D			Weather Condition F		
Q/U (g/m)	$(W/2)_{max}$ (m)		Q/U (g/m)	$(W/2)_{max}$ (m)	
1 500 000	3 370	(99.5 km)*	130 000	1 415	(99.5 km)*
1 250 000	3 010		125 000	1 375	
1 000 000	2 625		100 000	1 165	
750 000	2 195		75 000	940	
500 000	1 710		50 000	695	
300 000	1 245		25 000	415	
250 000	1 110		20 000	350	
200 000	970		15 000	290	
150 000	810		10 000	225	
125 000	725		7 500	190	
100 000	630		5 000	145	
75 000	540		2 500	95	→ $(W/2)_{max}$ = 95 m
50 000	425	Q/U = 2 285→	1 000	50	
25 000	285		500	35	
20 000	250		250	25	
15 000	210				
10 000	165				
5 000	110				
2 500	75				
1 000	45				
500	30				
250	20				

* Data are provided up to a maximum downwind hazard distance of 100 km.

Example: A spill releasing acetic anhydride vapour at the rate of $Q = 4.8 \times 10^3$ g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 2285 g/m which results in a maximum plume hazard half-width $(W/2)_{max}$ = 95 m.

Note: Above table is valid only for an acetic anhydride concentration of 10 x TLV®, or 0.22 g/m^3.

Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 8.

5.3.2.4 **Figure 16: Plume travel time versus travel distance.** Figure 16 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship = Ut for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined, which indicates how far downwind the plume has travelled.

5.3.3 **Sample Calculation.** The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid acetic anhydride. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of acetic anhydride were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution

Step 1: Quantity spilled is given, q = 20 tonnes

Step 2: Determine the pool radius (r) for a spill of 20 tonnes

- Use the observed (measured) pool radius if possible. If not, use the maximum radius calculated assuming a 2 mm spill thickness
- Radius (r) = 120 m ÷ 1000 = 0.12 km

Step 3: Calculate the vapour emission rate (Q) at T = 20°C

- From Figure 12, for r = 120 m and T = 20°C, Q = 4.8×10^3 g/s

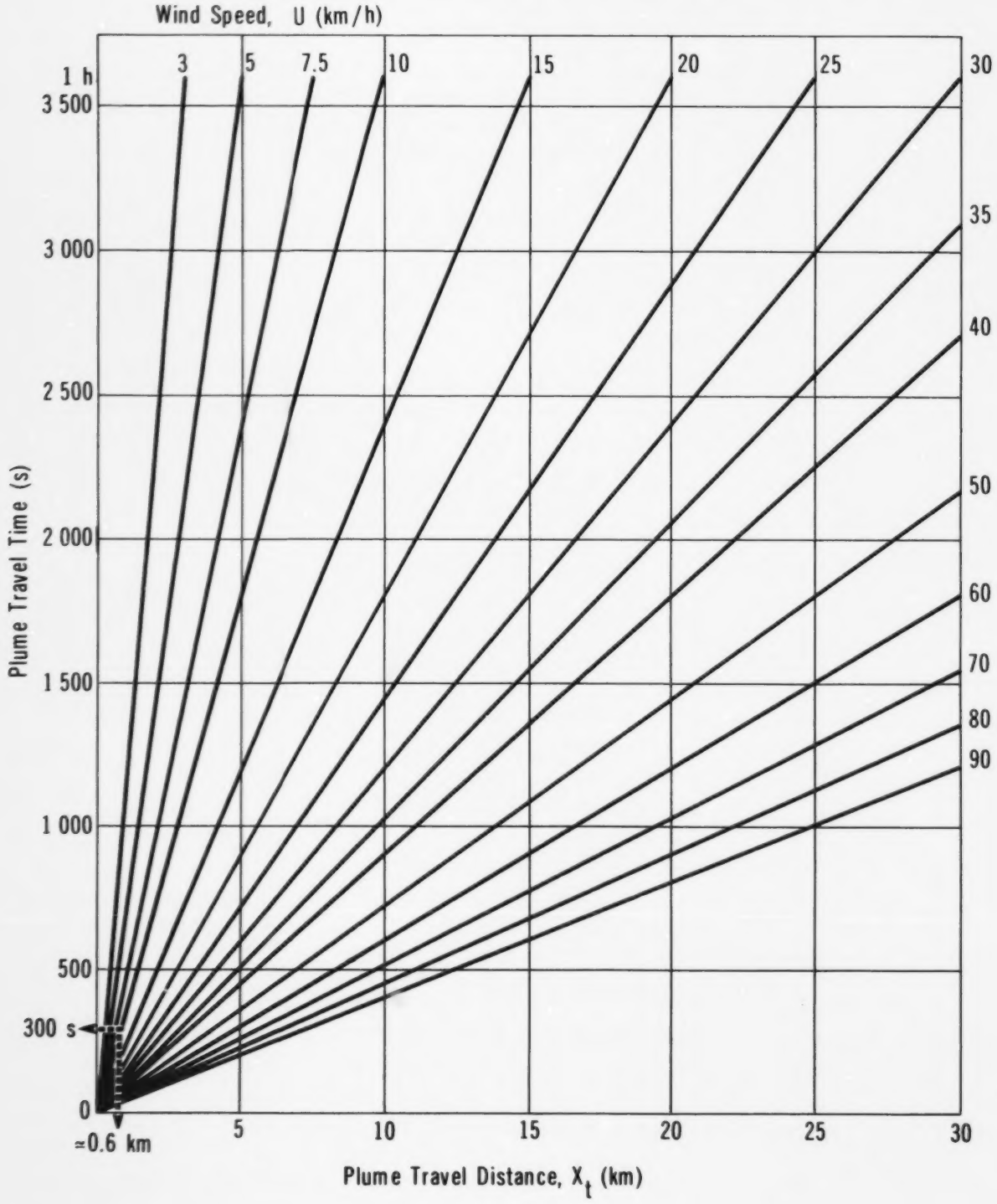
Step 4: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations

FIGURE 16

ACETIC ANHYDRIDE

PLUME TRAVEL TIME VS TRAVEL DISTANCE



- Given:
  U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s
  D = NW or 315° (D = Direction from which wind is blowing)

Step 5: Determine the weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL, so for acetic anhydride
  C = 0.22 g/m^3 (TLV® = 0.022 g/m^3; LFL = 120 g/m^3)

Step 7: Compute CU/Q

- $CU/Q = \frac{0.22 \times 2.1}{4.8 \times 10^3} = 9.6 \times 10^{-5}\ m^{-2}$

Step 8: Calculate the downwind distance (X_p) from the virtual point source

- From Figure 13, with CU/Q = 9.6 x 10^{-5} m^{-2} and weather condition F, $X_p \sim 3.8$ km

Step 9: Calculate the hazard distance (X_a) downwind of the area source

- With X_p = 3.8 km and r = 0.12 km, then
  $X_a = X_p - 10\,r$ = 3.8 km - 10 (0.12 km) = 2.6 km

Step 10: Calculate the plume hazard half-width $(W/2)_{max}$

- Use Table 8
- With Q = 4.8 x 10^3 g/s and U = 2.1 m/s
  then $Q/U = \frac{4.8 \times 10^3}{2.1} = 2285$ g/m
- Then for weather condition F the closest Q/U value is 2500 g/m, which gives $(W/2)_{max} \sim 95$ m

Step 11: Determine the time since the spill

- t = 5 min x 60 = 300 s

Step 12: Calculate the distance travelled (X_t) by the vapour plume since the time of the accident

- Using Figure 16, with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (95 m) by the maximum hazard distance downwind of the area source (2.6 km) along the direction of the wind, as shown in Figure 17
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 18
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 16 minutes before the plume reaches the maximum downwind hazard distance of 2.6 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, acetic anhydride will sink and react slowly, producing acetic acid and liberating heat. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water. As acetic anhydride is slightly denser than water, initially the maximum concentration would be expected near the bottom.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d < 100) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

FIGURE 17

ACETIC ANHYDRIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

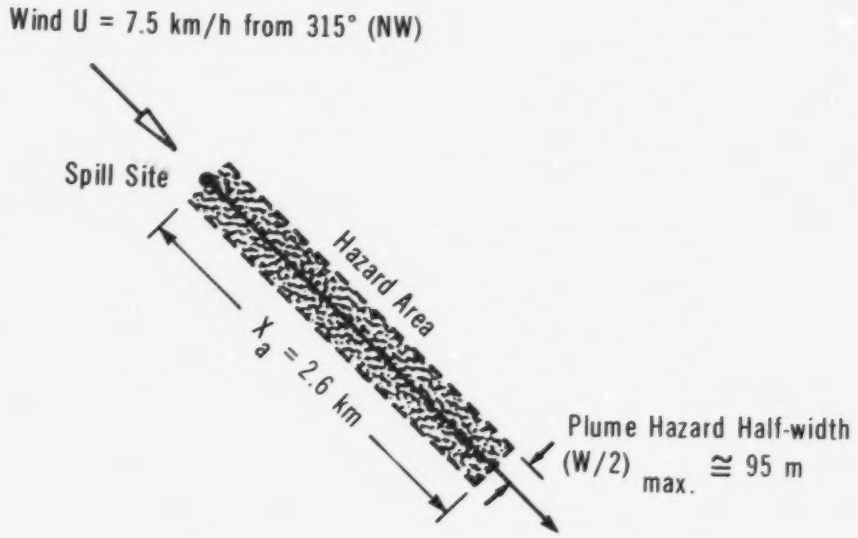
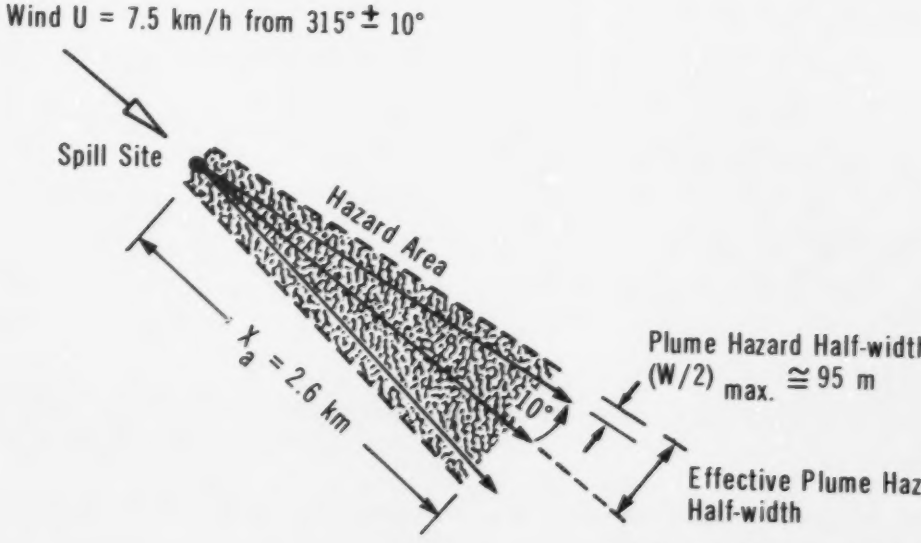


FIGURE 18

ACETIC ANHYDRIDE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



$= Xa \times 1000 \times \tan 10° + (W/2)_{max}$

$= 2.6 \times 1{,}000 \times \tan 10° + 95$ m

$=$ 550 m

5.4.2 Nomograms. The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

Figure 20: time versus distance for a range of average stream velocities

Figure 21: hydraulic radius versus channel width for a range of stream depths

Figure 22: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 23: alpha* versus diffusion coefficient for various time intervals

Figure 24: alpha versus delta* for a range of spill sizes

Figure 25: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 26: volume versus radius for the hazard zone for a range of lake depths

Figure 27: average concentration versus volume for the hazard zone for a range of spill sizes

The flow chart in Figure 19 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 20 through 27) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 20: Distance versus time. Figure 20 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 20.

Figure 21: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d).

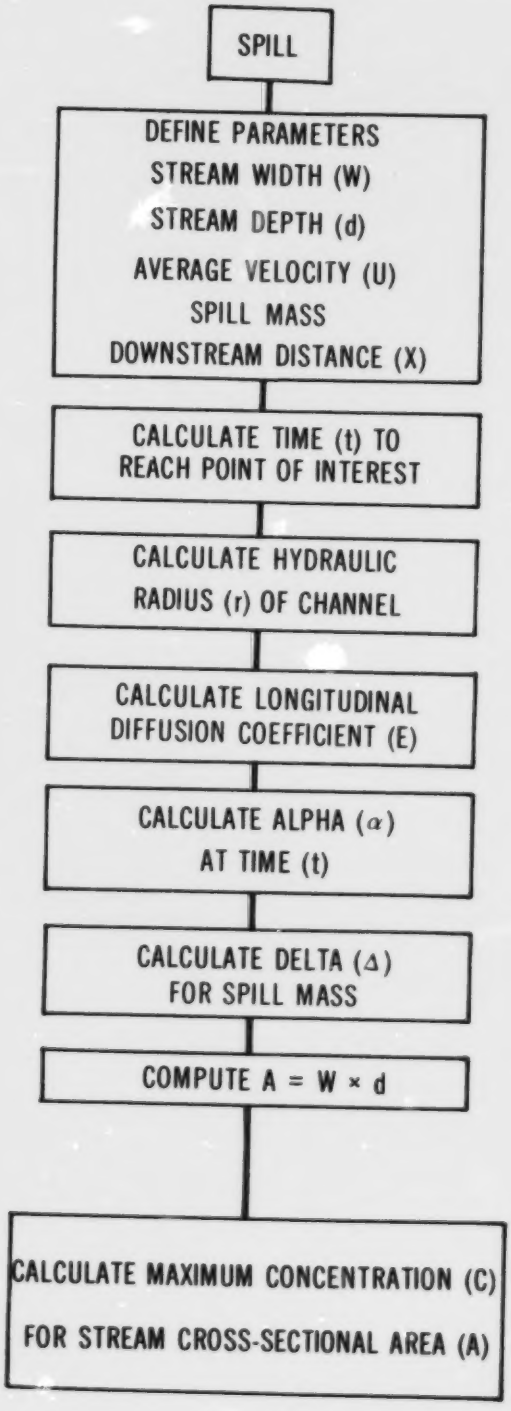
The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 21 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 19

ACETIC ANHYDRIDE

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

Step 2: Use Figure 20

t = _____ minutes

Step 3: Use Figure 21

r = _____ m

Step 4: Use Figure 22

E = _____ m^2/s

Step 5: Use Figure 23

α = _____

Step 6: Use Figure 24

Δ = _____

Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

Step 8: Use Figure 25

C = _____ ppm

FIGURE 20

ACETIC ANHYDRIDE

TIME vs DISTANCE

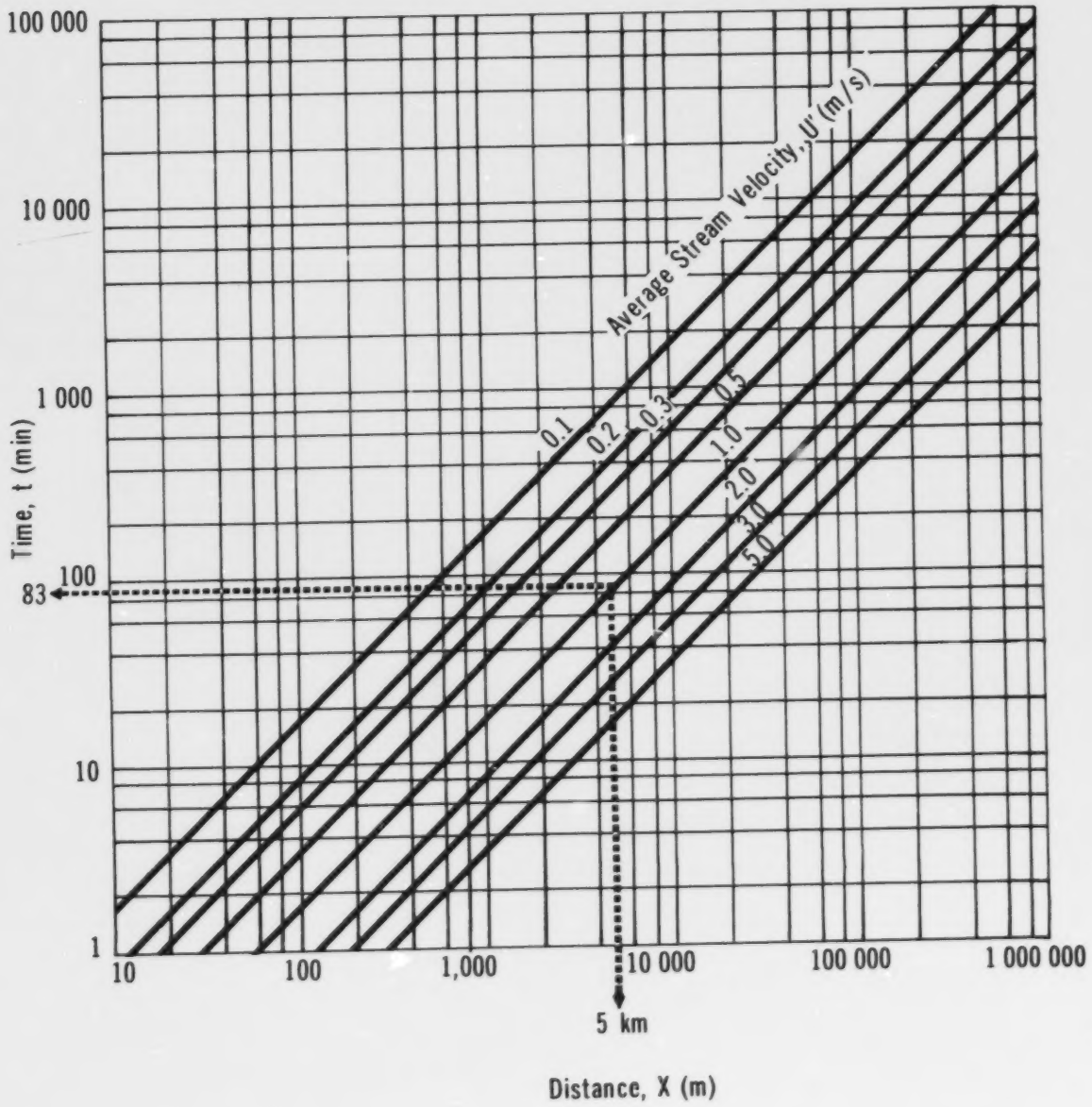


FIGURE 21

ACETIC ANHYDRIDE

HYDRAULIC RADIUS VS CHANNEL WIDTH

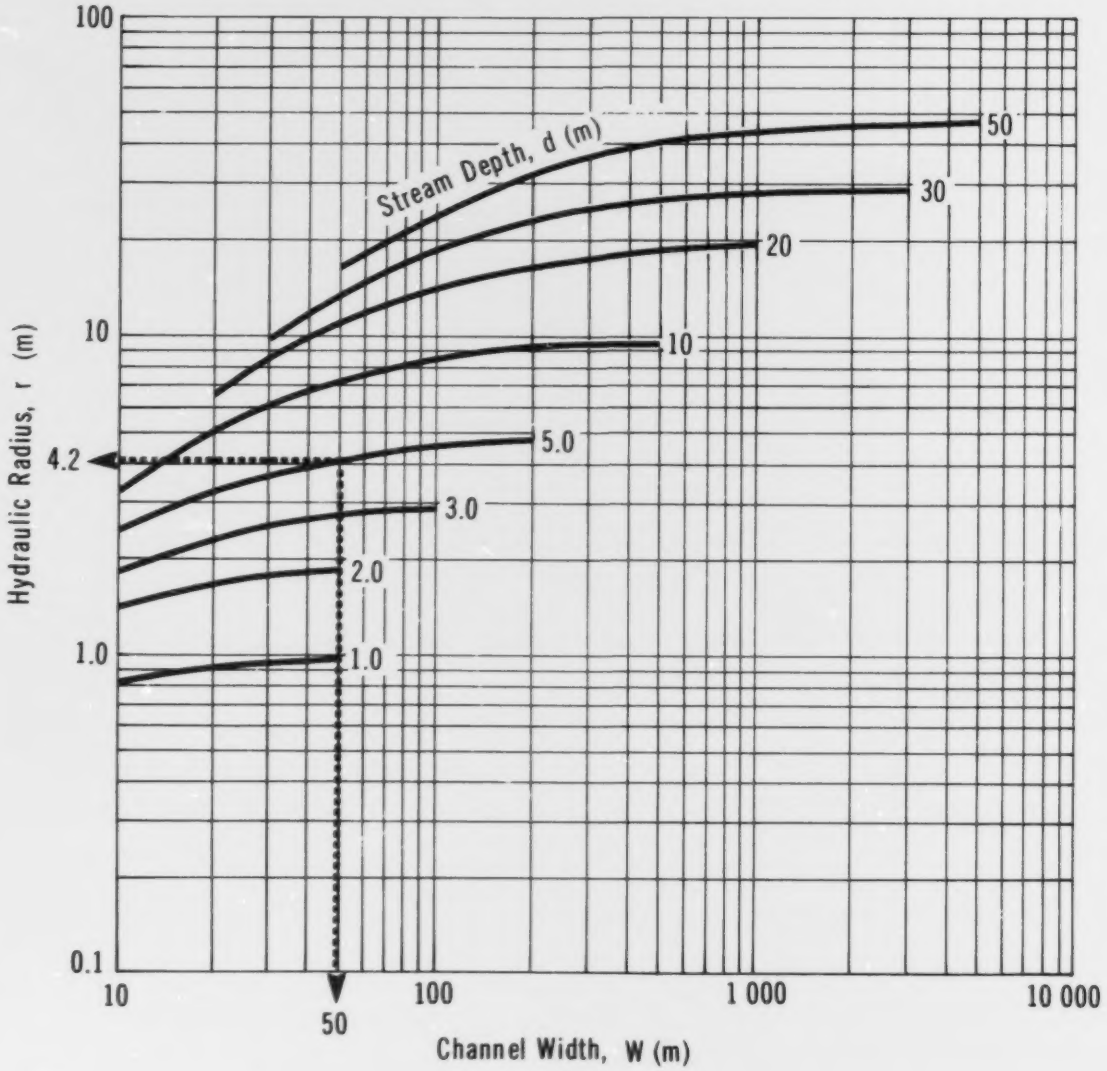


Figure 22: Diffusion coefficient versus hydraulic radius. Figure 22 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 21 and the average stream velocity (U).

Figure 23: Alpha versus diffusion coefficient. Figure 23 is used to estimate a conversion factor alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 24: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 24 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 25: Maximum concentration versus delta. Figure 25 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 25 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 26: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 26. The radius (r) represents the distance from the spill to the point of interest.

Figure 27: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 27 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of acetic anhydride has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

FIGURE 22

ACETIC ANHYDRIDE

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

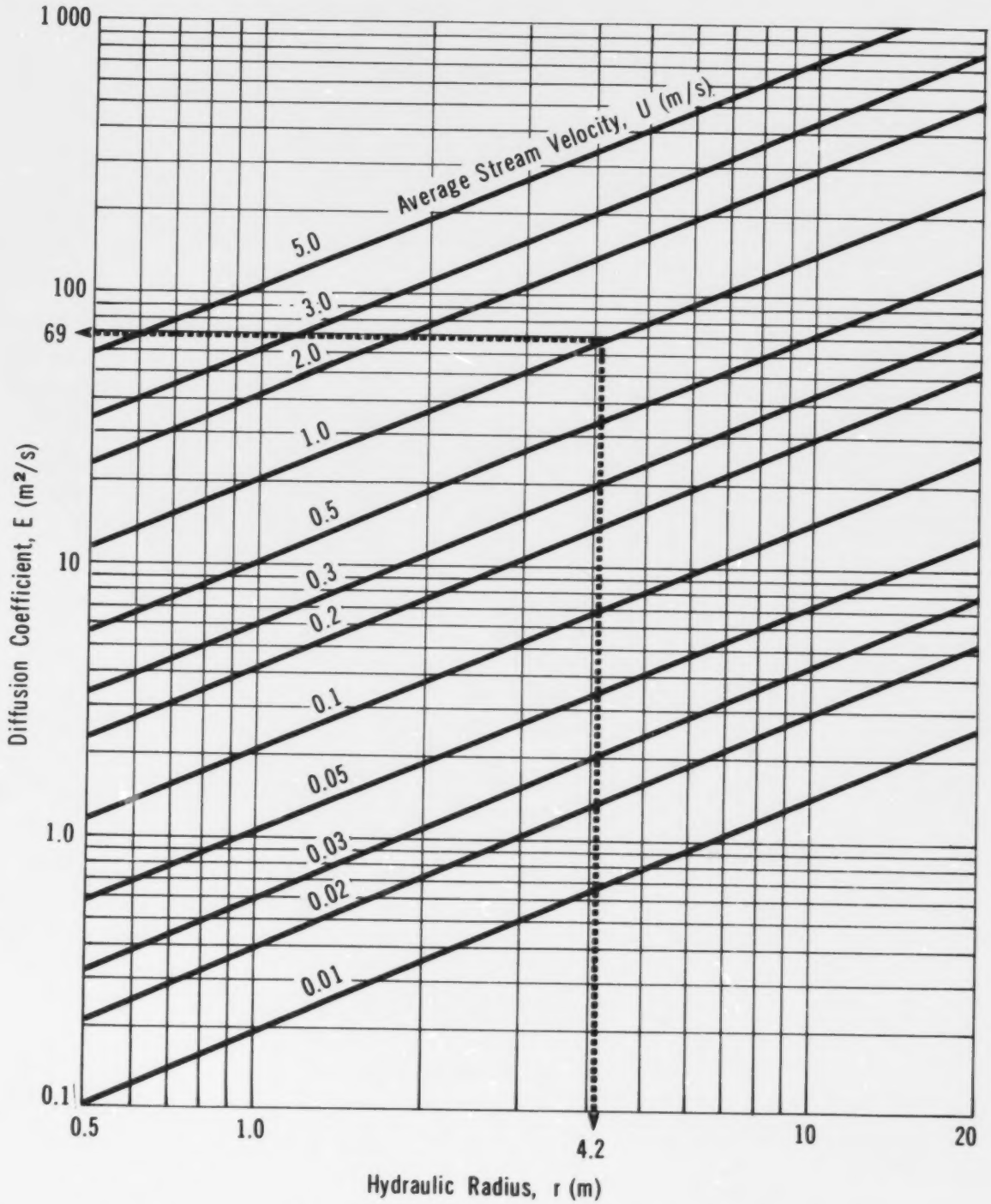


FIGURE 23

ACETIC ANHYDRIDE

ALPHA vs DIFFUSION COEFFICIENT

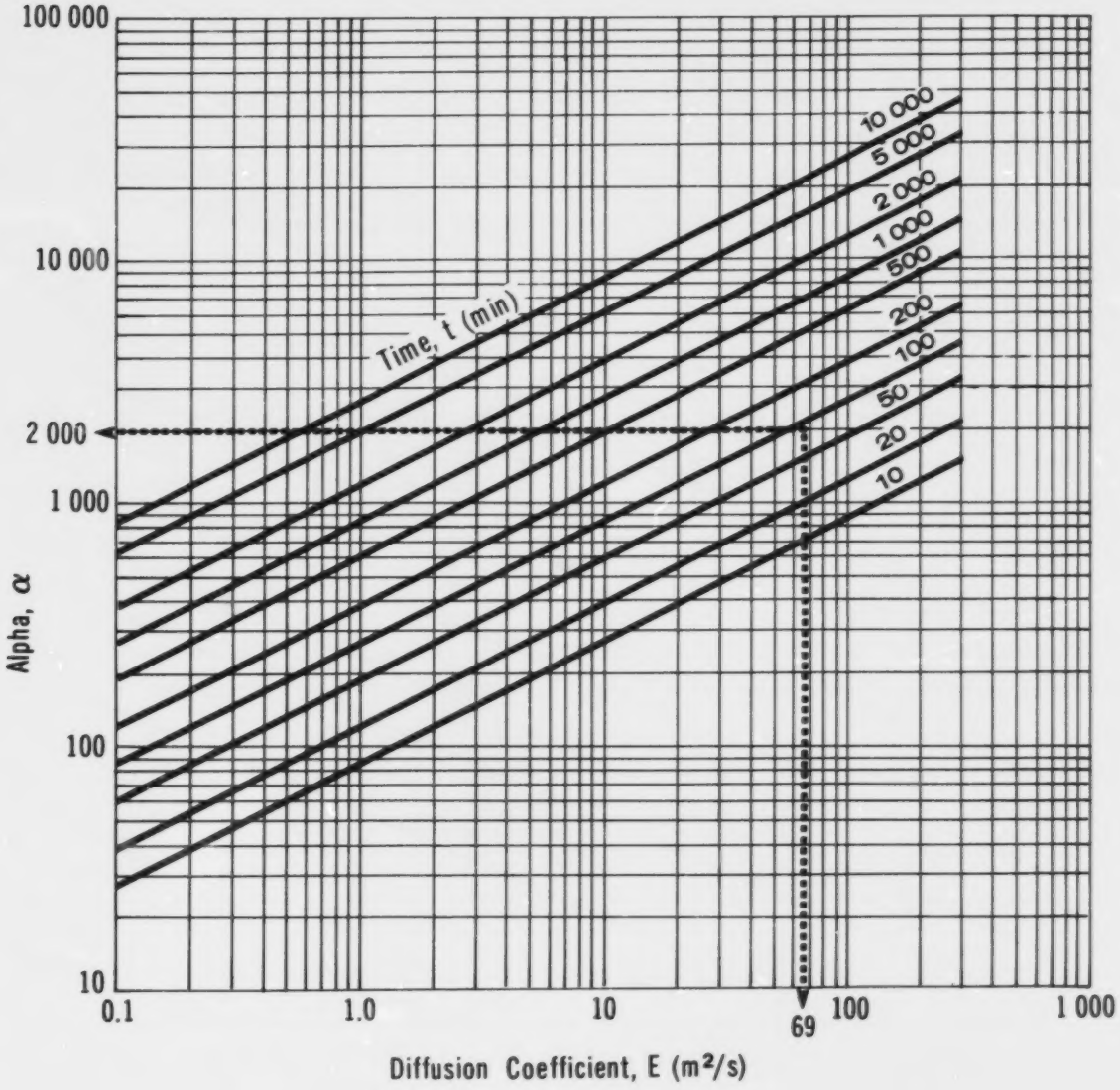


FIGURE 24

ACETIC ANHYDRIDE

ALPHA vs DELTA

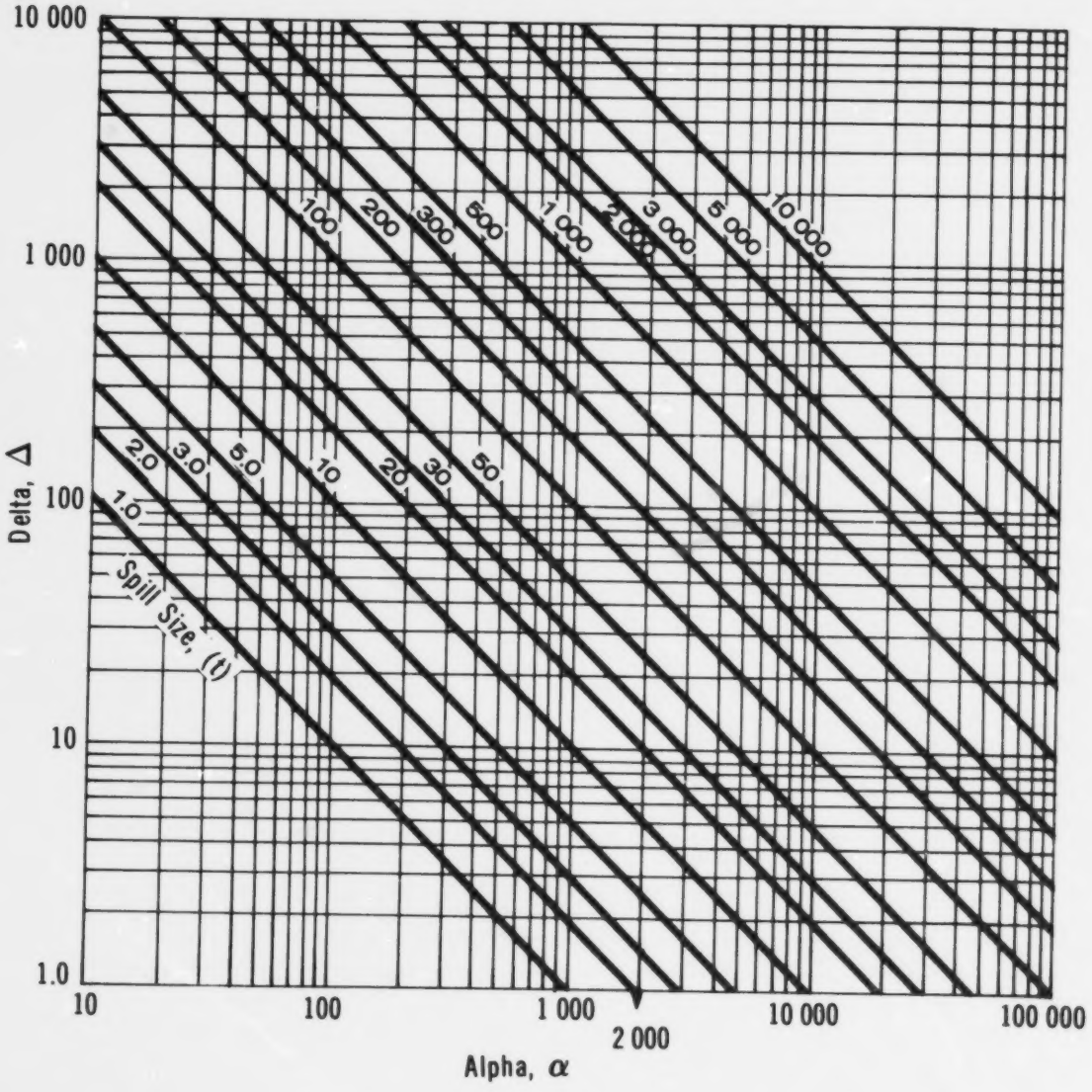


FIGURE 25

ACETIC ANHYDRIDE

MAXIMUM CONCENTRATION vs DELTA

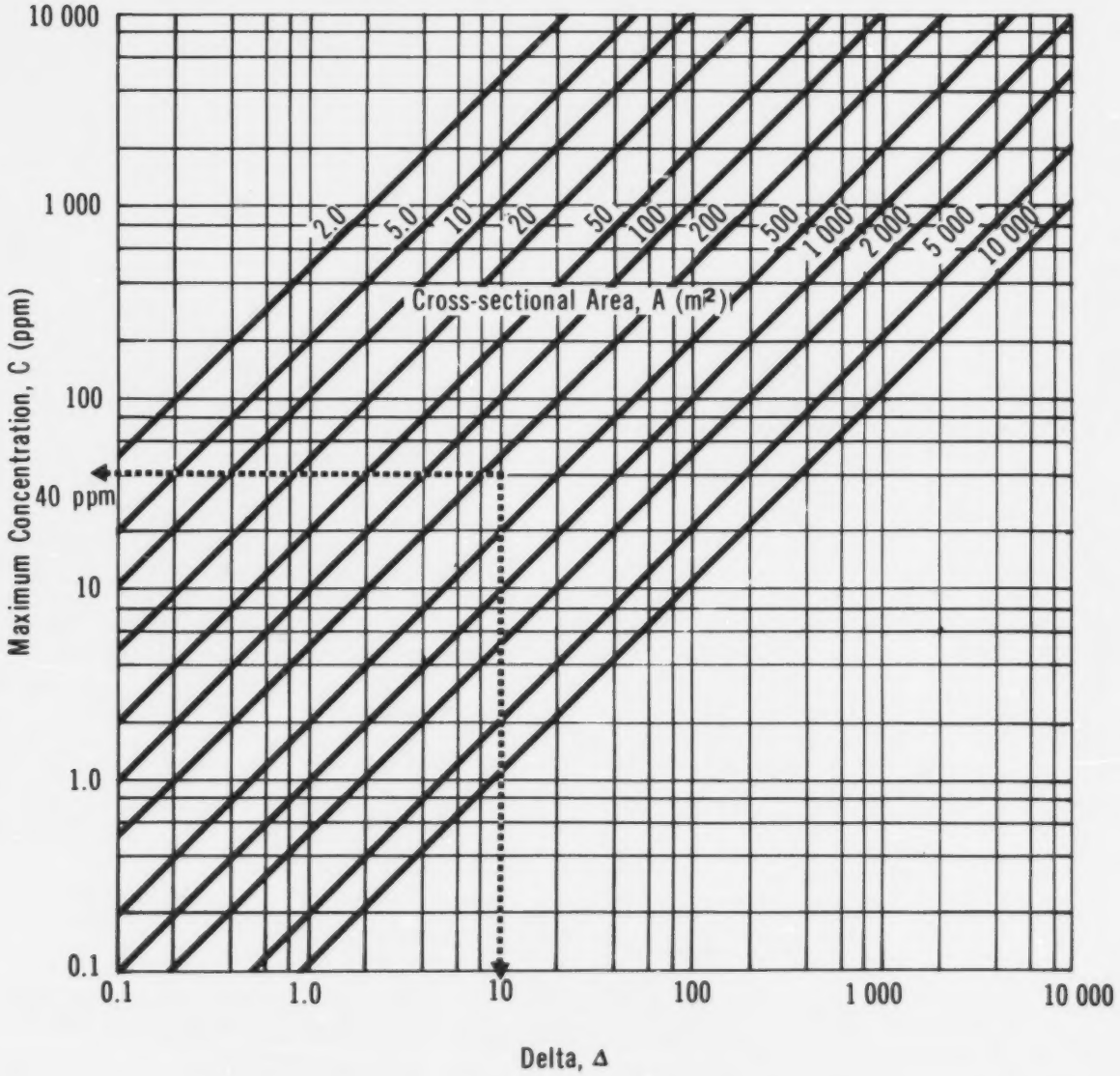


FIGURE 26

ACETIC ANHYDRIDE

VOLUME vs RADIUS

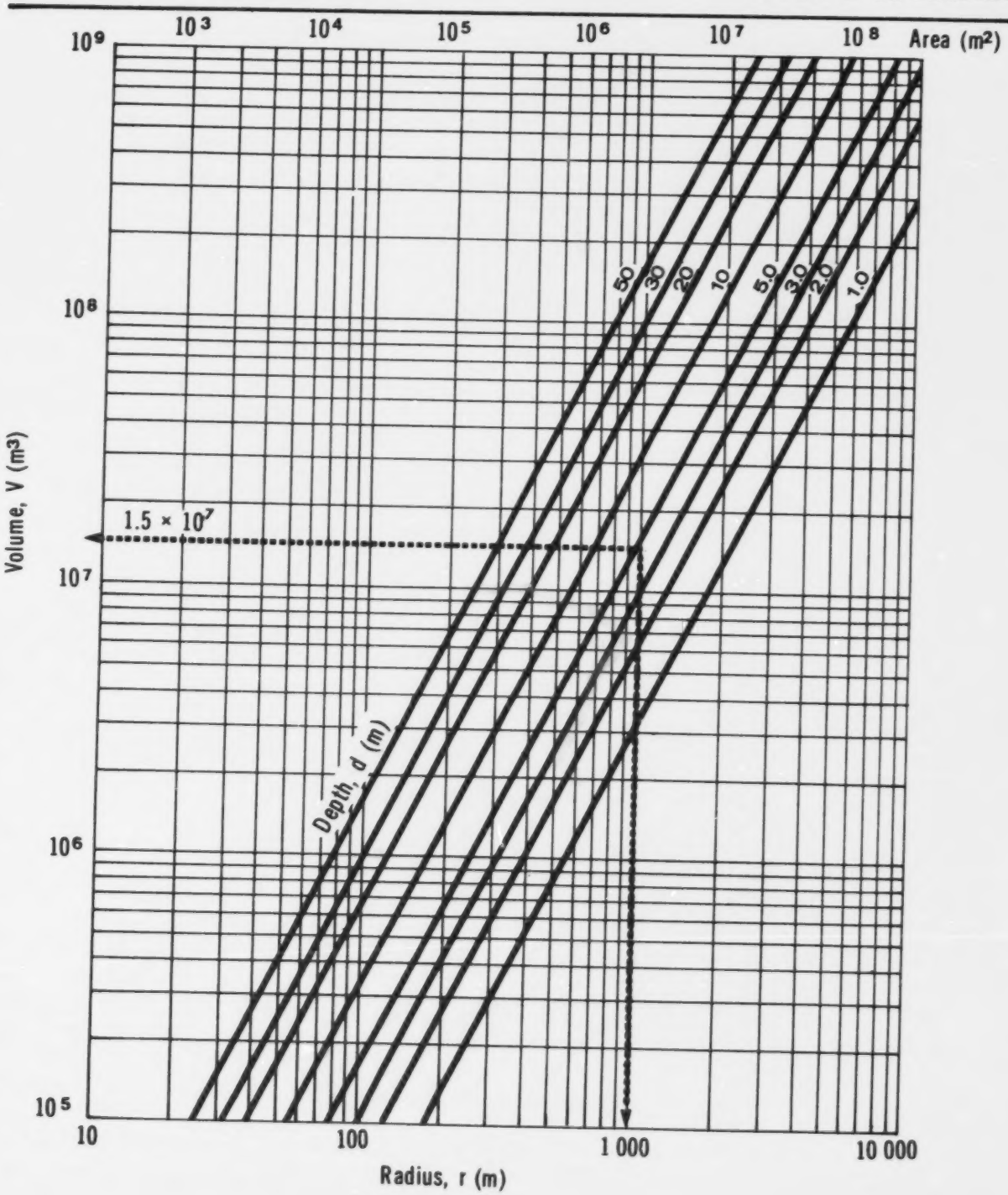
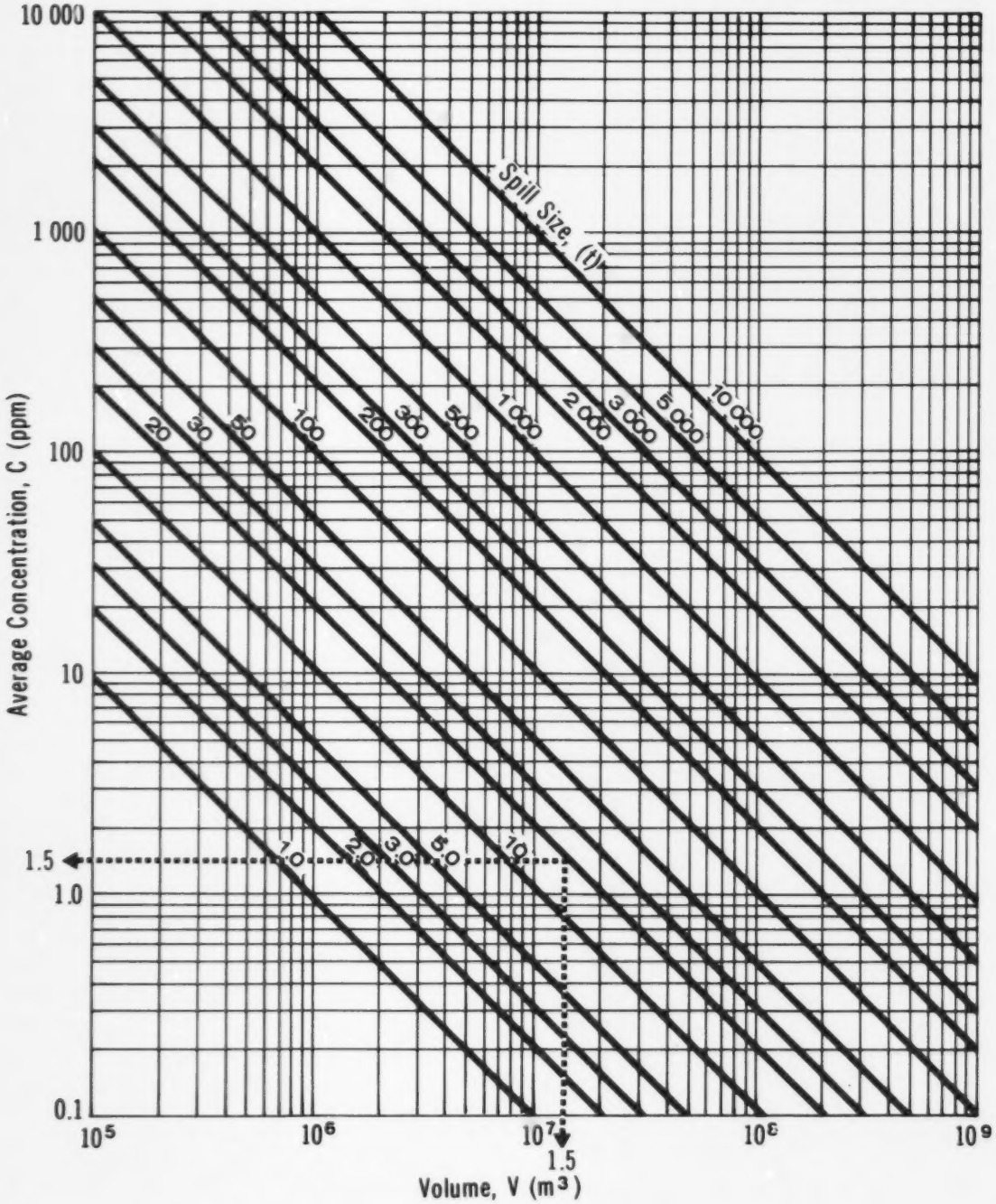


FIGURE 27

ACETIC ANHYDRIDE

AVERAGE CONCENTRATION vs VOLUME



Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- spill mass = 20 tonnes
- X = 5000 m

Step 2: Calculate the time to reach the point of interest

- Use Figure 20
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 21
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 22
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 23
- With E = 69 m^2/s and t = 83 min, (α) = 2000

Step 6: Calcualte delta (Δ)

- Use Figure 24
- With alpha (α) = 2000 and spill mass = 20 tonnes, delta (Δ) = 10

Step 7: Compute the stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate the maximum concentration (C) at the point of interest

- Use Figure 25
- With Δ = 10 and A = 250 m^2, C = 40 ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of acetic anhydride has occurred in a lake. The point of interest is located on the shore

approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill mass = 20 tonnes

Step 2: Determine the volume of water available for dilution

- Use Figure 26
- With r = 1000 m, d = 5 m, the volume is approximately 1.5×10^7 m^3

Step 3: Determine the average concentration

- Use Figure 27
- With V = 1.5×10^7 m^3 and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of acetic anhydride onto soil and its transport downward through the soil are presented here.

Acetic anhydride is shipped as a liquid, either pure or diluted to 78 percent by weight. When spilled onto soil, it will readily infiltrate downward toward the groundwater system.

Acetic anhydride reacts with water to produce acetic acid, with the liberation of much heat. Water present at the time of the spill, either from precipitation or flushing the site, will induce this reaction but will also serve to dilute the chemical.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or remain ponded. For this work, the soils have been assumed to be at field capacity (the maximum amount the soil can hold after excess is drained). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

During transport through the soil, acetic anhydride may react with some of the soil material through adsorption and ion exchange. However, significant amounts are expected to remain for transport down toward the groundwater table. The analysis used here neglects these retarding factors. Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and dispersion serving to reduce the concentrations. This is shown schematically in Figure 28.

5.5.2 Equations Describing Acetic Anhydride Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Acetic Anhydride in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa·s)

g = acceleration due to gravity = 9.81 m/s^2

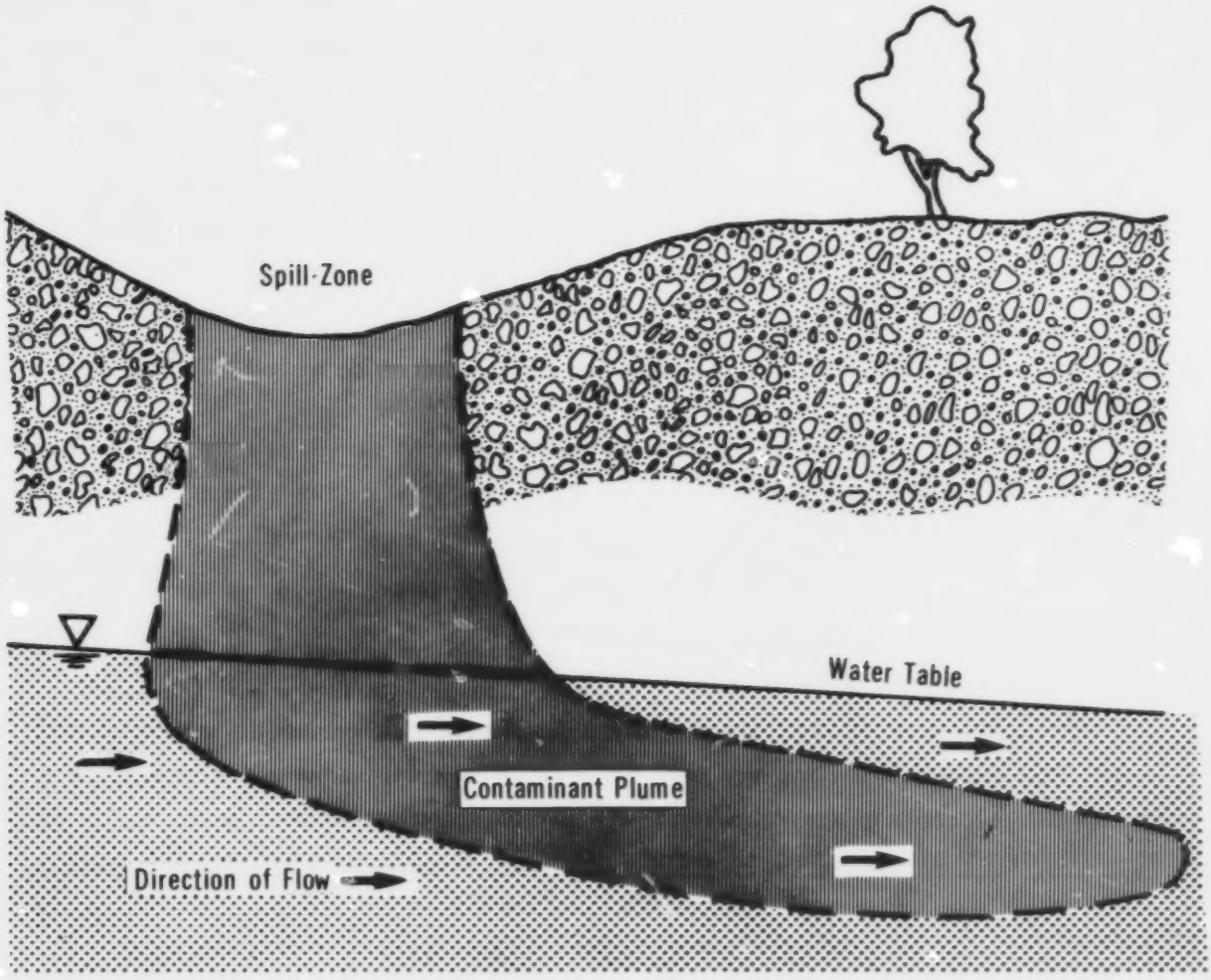
The fluids involved are pure and 10 percent by weight acetic anhydride, and water. The water calculations represent the extreme as acetic anhydride is diluted. The appropriate properties of acetic anhydride are given in the chart below:

	Acetic Anhydride				
	Pure		10% by Wt.		Water
Property	20°C	4°C	20°C	4°C	20°C
Mass density (ρ), kg/m^3	1078	1104	1006	1010	1000
Absolute viscosity (μ), Pa·s	0.86×10^3	1.17×10^3	0.99×10^3	1.53×10^3	1.0×10^3
Saturated hydraulic conductivity (K_o), m/s	$(1.2 \times 10^7)k$	$(0.93 \times 10^7)k$	$(1.0 \times 10^7)k$	$(0.65 \times 10^7)k$	$(0.98 \times 10^7)k$

FIGURE 28

ACETIC ANHYDRIDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of acetic anhydride into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flowchart for the use of the nomograms is presented in Figure 29. The nomograms are presented as Figures 30, 31 and 32. The water line on the nomograms represents the maximum penetration of water at 20°C, in time t_p. It is a limiting condition as acetic anhydride becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of acetic anhydride has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 12 minutes after the spill.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 12 min

Step 2: Calculate the area of the spill

- $A = \pi r^2 = 232\ m^2$

FIGURE 29

ACETIC ANHYDRIDE

FLOWCHART FOR NOMOGRAM USE

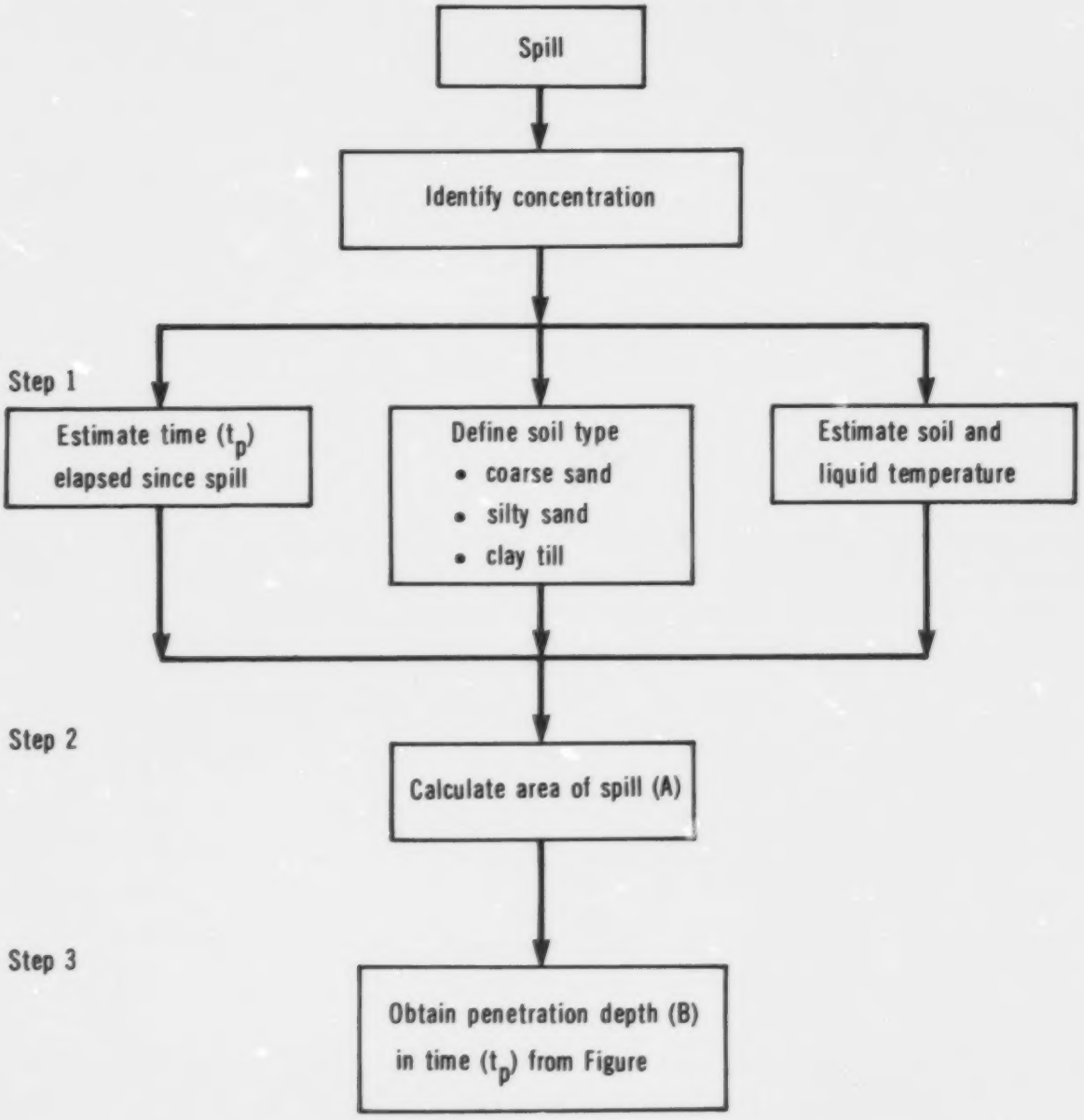


FIGURE 30

ACETIC ANHYDRIDE

PENETRATION IN COARSE SAND

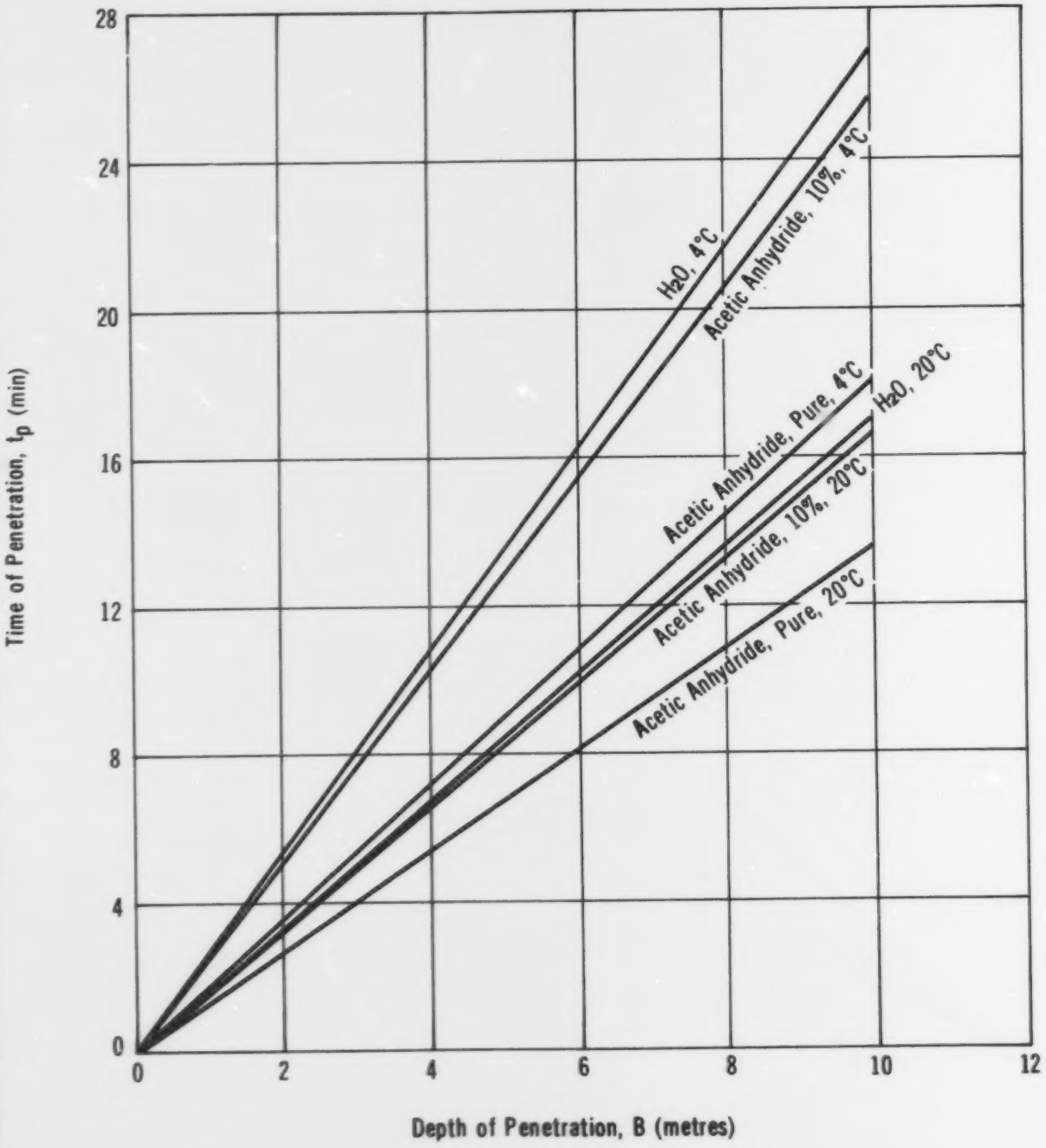


FIGURE 31

ACETIC ANHYDRIDE

PENETRATION IN SILTY SAND

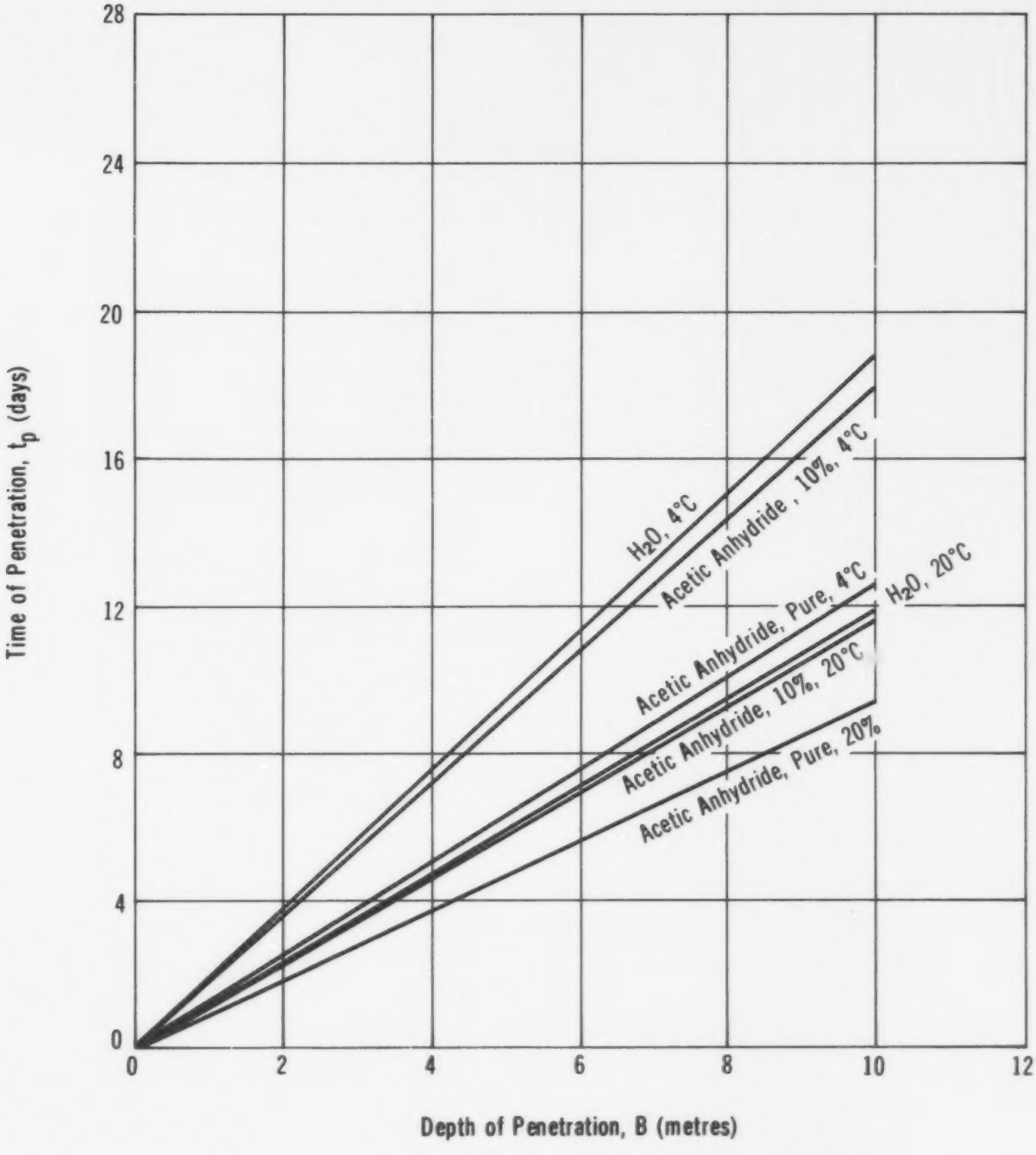
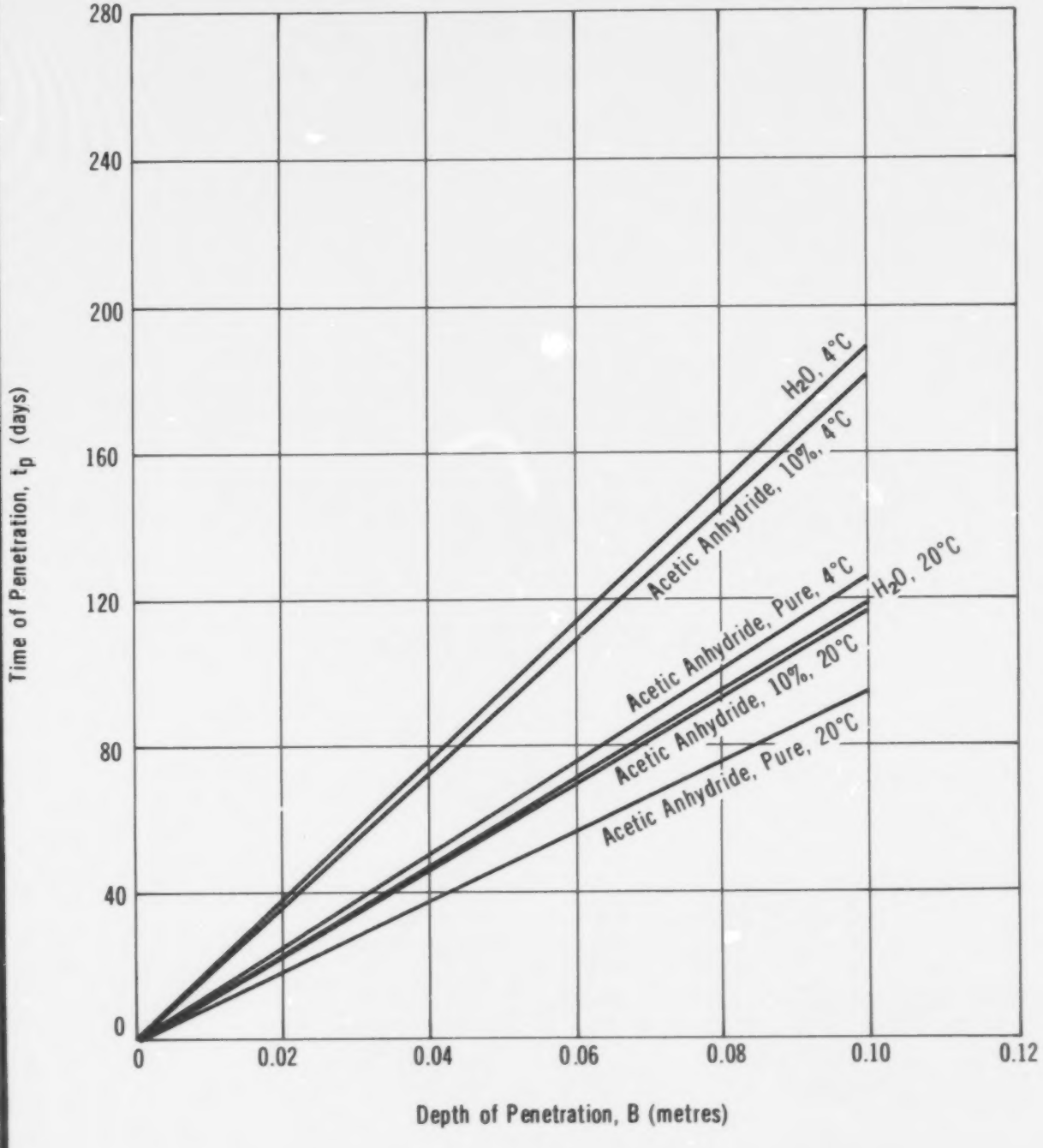


FIGURE 32

ACETIC ANHYDRIDE

PENETRATION IN CLAY TILL



Step 3: Estimate the depth of penetration (B) at time (t_p)

- For coarse sand, B = 8.8 m at t_p = 12 min
- Groundwater table has not been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. In the United States, a "tolerable" limit of 104 ppm has been recommended (OHM-TADS 1981). A guideline of 1 mg/L has been recommended in Europe (MHSSW 1976).

6.1.2 Air. Canadian environmental regulations do not specify a limit for acetic anhydride.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Acetic anhydride hydrolyzes to acetic acid in water. Like acetic acid, it has been assigned a TL_m96 of 10 to 100 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity. The following data are for acetic acid except where noted. Acetic acid is produced when acetic anhydride enters water.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
50	24	Brook trout	lethal	-	WQC 1963
114	24	Minnow	lethal	-	WQC 1963
423	20	Goldfish	lethal	-	Verschueren 1984
Microorganisms (Acetic Anhydride)					
1150		Bacteria (*Pseudomonas putida*)	inhibition of cell multi-plication		Verschueren 1984
3400		Green algae (*Scenedesmus quadricauda*)	inhibition of cell multi-plication		Verschueren 1984
30		Protozoa (*Entosiphon sulcatum*)	inhibition of cell multi-plication		Verschueren 1984

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
360		Algae (*Chlorella pyranoidosa*)	toxic		Verschueren 1984

6.2.2.2 Saltwater toxicity (acetic acid).

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
32	48	Brine shrimp	TL_m	static	Price 1974
100 to 300	48	Shrimp	LC_{50}	aerated	Portman 1970
42	24	Brine shrimp	TL_m	static	DPIMR 1983
>100	96	Shore crab (*Carcinus maenus*)	LC_{50}	continuous flow	WQCDB-5 1973
>100	96	Brown Shrimp (*Crangon crangon*)	LC_{50}	continuous flow	WQCDB-5 1973
6	-	Amphipod (*Limnea ovata*)	perturbation level	-	Verschueren 1984
14	-	Amphipod (*Gammarus pulex*)	perturbation level	-	Verschueren 1984
Fish Toxicity Tests					
>100	72	Fathead minnow	no toxic effect	50°F	EPA 440/9-75-009
100	96	Goldfish	TL_m		Little 1970
100 to 200	96	Creek chub	TL_m	Detroit river water	Little 1970
75	96	Bluegill	TL_m		Cairns 1968
75	96	Sunfish	TL_m	18-20°C, soft water	WQC 1963
286	24	Goldfish	LC_{50}	-	DPIMR 1983
270	72	Channel catfish	TL_m	25°C	DPIMR 1983
251	24-96	Mosquito fish	TL_m	turbid	DPIMR 1983
624	72	Channel catfish	LC_{100}	25°C	DPIMR 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
175	1	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, reconstituted water	Mattson 1976
106	24-48	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, reconstituted water	Mattson 1976
79	72-96	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, reconstituted water	Mattson 1976
>315	1	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, Lake Superior water	Mattson 1976
122	24	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, Lake Superior water	Mattson 1976
92	48	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, Lake Superior water	Mattson 1976
88	72-96	Fathead minnow	LC_{50}	18-22°C, pH < 5.9, Lake Superior water	Mattson 1976
Invertebrates					
80-150	120	Daphnia	immobilized	Lake Erie	WQCDB-5 1973
47	24	*Daphnia magna*	TL_m	-	Verschueren 1984
Microorganisms					
74	-	Diatom (*Navicula semtnulum*)	50% reduction in growth	soft water, 20°C	DPIMR 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
>4	12	Algae (*Nitzschia linearis*)	LC_{50}	-	DPIMR 1983
74	-	Algae (*Nitzschia linearis*)	LC_{50}	synthetic water	WQCDB-5 1973
2850	-	Bateria (*Pseudomonas putida*)	inhibition of cell multi-plication	-	Verschueren 1984
90		Algae (*Microcystis aeruginosa*)	inhibition of cell multi-plication		Verschueren 1984
4000		Green algae (*Scenedesmus quadricauda*)	inhibition of cell multi-plication		Verschueren 1984
1350		Protozoa (*Uronema parduczi*)	inhibition of cell multi-plication		Verschueren 1984
78		Protozoa (*Entosiphon sulcatum*)	inhibition of cell multi-plication		Verschueren 1984
350		*Chorella pyranoidosa*	toxic		Jones 1971

6.3 Effect Studies

The toxicity of acetic acid to an insect (mosquito larvae, *Culex* sp.) in water has been determined to be 1500 mg/L in 24 hours (Verschueren 1984).

The effect of acetic acid vapour on a number of plant species has been determined. The 2-hour EC_{50} (for visible leaf damage) is as follows (Verschueren 1984):

Plant	EC_{50} (ppm)
Wheat	9.3
Alfalfa	3.1
Tobacco	16.5

Plant	EC_{50} (ppm)
Soybean	8.1
Corn	20.1

6.4 Degradation

6.4.1 Biochemical Oxygen Demand (as acetic acid).

B.O.D. kg/kg	B.O.D. % Theor.	Time (days)	Seed	Method	Reference
>1	66	5	Sewage seed	Salt water	Price 1974
>1	88	10	Sewage seed	Salt water	Price 1974
>1	100	20	Sewage seed	Salt water	Price 1974
>1	76	5	Sewage seed	Fresh water	Price 1974
>1	82	10	Sewage seed	Fresh water	Price 1974
>1	85	15	Sewage seed	Fresh water	Price 1974
>1	96	20	Sewage seed	Fresh water	Price 1974
>1	50	0.5	Phenol-acclimated activated sludge	-	DPIMR 1983
>1	53	1-5	Activated sludge	Respirometer	DPIMR 1983
0.7	-	5	-	-	DPIMR 1983
0.9	-	20	-	-	DPIMR 1983
0.34-0.88	-	5	Sewage seed	-	DPIMR 1983
1	-	-	Chemical	C.O.D.	DPIMR 1983

The Chemical Oxygen Demand is approximately 1 kg oxygen/kg acetic acid (Jones 1971). Oxygen deficiencies may result from rapid biochemical and chemical oxygen demand. High concentrations may cause extremely low pH, killing biota and interfering with coagulation (OHM-TADS 1981).

6.5 Long-term Fate and Effects

Natural waters will neutralize dilute solutions to acetate salts. Acetic anhydride shows no potential for biological accumulation or food chain contamination (OHM-TADS 1981).

7 HUMAN HEALTH

Acetic anhydride is a colourless, mobile and strongly refractive chemical under normal temperature and pressure conditions. Its odour is strong, pungent, and vinegar-like. The vapour is sufficiently irritating to the eyes, nose and throat at concentrations below the current exposure standards that acetic anhydride is considered to have good warning properties (AAR 1981).

The compound is highly reactive. In the presence of warm water or steam, acetic anhydride decomposes to acetic acid and may give off large amounts of heat in this process (GE 1980). Much of its destructive effects in contact with human tissue may be a result of this reaction and the formation of acetic acid on the skin. The recommended TLV® of 5 ppm has been developed by analogy to the irritant effects caused by exposure to acetic acid (Doc. TLV 1981). While no cumulative effects in relation to humans were reported in the literature, acetic anhydride is being considered for carcinogenicity bioassay due to the significant potential human exposure to the compound (USDHEW 1980).

No recent monographs on the toxic effects of exposure to the compound were found in the literature. There were no reports concerning the mutagenic or teratogenic effects of the compound.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. With the exception of data pertaining to mutagenicity, teratogenicity and carcinogenicity, only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for acetic anhydride are based upon an analogy with acetic acid, and upon preventing undue irritation (Doc. TLV 1981). Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h) ceiling	USA-ACGIH	5 ppm (~20 mg/m^3)	TI V 1983

Guideline (Time)	Origin	Recommended Level	Reference
PEL (8 h)	USA-OSHA	5 ppm (~20 mg/m^3)	NIOSH/OSHA 1981
Permissible concentration (8 h)	B.C.	5 ppm (20 mg/m^3)	B.C. 1980
8 h average concentration limit	Saskatchewan	20 mg/m^3	Sask. 1981
Short-term Exposure Limits (STEL)			
Ceiling	USA-ACGIH	5 ppm (~20mg/m^3)	TLV 1983
15 min average contamination limit	Saskatchewan	20 mg/m^3	Sask. 1981
Other Human Toxicities			
IDLH	USA-NIOSH/OSHA	1000 ppm	NIOSH Guide 1978

Inhalation Toxicitiy Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV®, in ppm)

At 36°C, ITI = 1315.12 (9.75 mm Hg/5 ppm)

At 36°C, ITI = 2.6 x 10^3

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Liquid causes skin burns	Doc. TLV 1981
Unspecified	Causes severe burning sensation when in contact with the skin. If acetic anhydride is not removed by washing, skin may	NIOSH/OSHA 1981

Exposure Level (and Duration)	Effects	Reference
	become reddened and subsequently white and wrinkled. Skin burns may appear later	
Unspecified	Can cause contact dermatitis. Hypersensitivity dermatitis may occasionally develop	USDHEW 1977
SPECIES: Rabbit		
4000 mg/kg	LD_{50}	TDB (on-line) 1981
10 mg/kg (24 h)	Mild irritation	RTECS 1979
540 mg	On open skin causes mild irritation	RTECS 1979

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
"High concentrations"	Vapour may cause conjunctivitis, photophobia, lacrimation, conjunctival edema and corneal burns which may develop into temporary or permanent interstitial keratitis with corneal opacity due to progression of infiltration	USDHEW 1977
Unspecified (small amounts of liquid)	Contamination of the eye by small amounts of liquid causes burning discomfort followed some hours later by an increasingly severe reaction, with corneal and conjunctival edema. Interstitial corneal opacity may develop	TDB (on-line) 1981
Unspecified	Contact with the liquid or vapour may produce a serious eye burn. Immediately after contact, a burning sensation of the eyes with tearing occurs. This may be followed later by impairment of	NIOSH/OSHA 1981

Exposure Level (and Duration)	Effects	Reference
	vision. After exposure, there may be a delay in the appearance of severe eye burns	
Unspecified	May penetrate intact corneal epithelium rapidly and reach the iris in concentrations high enough to cause iritis	Doull 1980
Unspecified	Physiological effects generally resemble those of corresponding acid, but it is a more potent eye irritant in the vapour phase and may produce chronic conjunctivitis	TDB (on-line) 1981
Unspecified	Permanent scars may appear in cornea	TDB (on-line) 1981
Unspecified	Eye irritation. Severe lacrimator	Doc. TLV 1981
0.08 ppm	Eyes affected, threshold level	Kirk-Othmer 1978
SPECIES: Rabbit		
250 µg	Severe irritation	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristics: Very strong; pungent; vinegar- or sour acid-like characteristics (AAR 1981).

Odour Index: 14 611 (Verschueren 1984).

Parameter	Media	Concentration	Reference
Odour Perception Threshold		0.14 ppm	Verschueren 1984
50 Percent Recognition Threshold		0.36 ppm	Verschueren 1984
100 Percent Recognition Threshold		0.36 ppm	Verschueren 1984

7.3.2 Taste. Taste Characteristics: Pungent, vinegar-like (AAR 1981).

Parameter	Media	Concentration	Reference
Upper Taste Threshold	In water	1000 ppm - acetic acid	DPIMR 1981
Lower Taste Threshold	In water	300 ppm - acetic acid	DPIMR 1981

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
"High concentrations"	Severe damage to the lungs and delayed breathing difficulties may occur	NIOSH/OSHA 1981
Unspecified	Eye, nose and throat irritation. Bronchial and lung injury were likely to occur from inhalation of acetic anhydride vapour	Doc. TLV 1981
Unspecified	Marked lacrimator; unlikely to find systemic effects	Doc. TLV 1981
Unspecified	No cumulative effects are known	Doc. TLV 1981
0.04 ppm	Affects electroencephalogram patterns	Kirk-Othmer 1978
SPECIES: Rat		
2000 ppm (4 h)	LC_{100}	Verschueren 1984
1000 ppm (4 h)	LC_{LO}	DPIMR 1981
Chronic Exposures		
SPECIES: Human		
Unspecified ("repeated or prolonged exposure")	May cause irritation of the skin and chronic eye irritation. Allergic sensitization of the skin may occur	NIOSH/OSHA 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
1.78 g/kg	LD_{50}	Doc. TLV 1981

7.4.3 Percutaneous. Only systemic effects due to percutaneous exposures are reported here.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
4000 mg/kg	LD_{50}	RTECS 1979

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
Unspecified	Requested carcinogenesis bioassay by NCI. No selection has been reported	USDHEW 1980

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their source indicated.

7.5.1 Inhalation.

1. "Irritating vapours (sic) usually force workers out of danger before injury occurs" (AAR 1981).
2. Irritates mucous membranes of the mouth and respiratory tract.
3. Burning sensation.
4. Lacrimation
5. Coughing.
6. Nausea and vomiting.
7. Corrosive action on contact with tissue (DPIMR 1981).

7.5.2 Ingestion.

1. Intense thirst (TDB (on-line) 1981).
2. Clammy skin (TDB (on-line) 1981).
3. Weak and rapid pulse (TDB (on-line) 1981).
4. Shallow respiration (TDB (on-line) 1981).
5. Scanty urine (TDB (on-line) 1981).
6. Severe irritation of mouth, nose, throat and stomach.
7. Burning pain in stomach.
8. Nausea and vomiting.
9. Corrosion of mucous membranes of the nose, mouth, throat and esophagus accompanied by pain and dyspnea (TDB (on-line) 1981).
10. Necrotic area, first greyish white in colour, becoming blackened and discoloured (TDB (on-line) 1981).
11. Circulatory collapse (TDB (on-line) 1981).
12. Shock (TDB (on-line) 1981).
13. Glottal edema (TDB (on-line) 1981).
14. Death (TDB (on-line) 1981).

7.5.3 Skin Contact.

1. Burning sensation.
2. Initial reddening of affected area followed by a wrinkling and whitening.
3. Dermatitis (USDHEW 1977).
4. Allergic sensitization (NIOSH/OSHA 1981).
5. Burns.

7.5.4 Eye Contact.

1. Burning sensation.

2. Lacrimation.
3. Photophobia (USDHEW 1977).
4. Interstitial keratitis with corneal opacity (USDHEW 1977).
5. Corneal and conjunctival edema (TDB (on-line) 1981).
6. Serious eye burns.
7. Impairment of vision.
8. Iritis (Doull 1980).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Acetic Anhydride with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire		•	•										Vapours form explosive mixture with air	Sax 1979; NFPA 1978
Heat		•				•							Flammable liquid. Emits toxic fumes (ketene) when heated to decomposition	Sax 1979
Water/Steam			•							•			Reacts to produce acetic acid and heat	Sax 1979; Bretherick 1979
SPECIFIC CHEMICALS														
2-Aminoethanol	•							•					In a closed container	NFPA 1978
Aniline	•							•					In a closed container	NFPA 1978
Barium Peroxide		•	•										Produces acetyl peroxide	Bretherick 1979
Boric Acid			•										Explosion at 60°C	Bretherick 1979
Chlorosulphonic Acid	•							•					In a closed container	NFPA 1978

8.1 Compatibility of Acetic Anhydride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Chromium Trioxide (Chromic Acid) (Chromic Anhydride)		•								•			Violent explosion can occur	Bretherick 1979; NFPA 1978
1,3-Diphenyl-triazene		•								•			Violently explosive on heating	Bretherick 1979
Ethylene Diamine	•							•					In a closed container	NFPA 1978
Ethyleneimine	•							•					In a closed container	NFPA 1978
Hydrochloric Acid	•		•					•					Explosive hydrolysis, heat and pressure rise in a closed container	Bretherick 1979; NFPA 1978
Hydrofluoric Acid	•							•					In a closed container	NFPA 1978
Hydrogen Peroxide		•											Excess of anhydride can produce diacetyl peroxide which is unstable	NFPA 1978
Hypochlorous Acid		•								•				Bretherick 1979

8.1 Compatibility of Acetic Anhydride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Glycerol									•				Violent reaction in presence of phosphorus oxychlorine	NFPA 1978
Nitric Acid	•	•								•			Pressurization in a closed container; under certain conditions explodes on contact	Bretherick 1979; Leleu 1972
Nitrogen Peroxide		•								•			Violent explosion	NFPA 1978
Oleum	•						•						In a closed container	NFPA 1978
Perchloric Acid	•	•								•			Violent exothermic hydrolysis leading to explosion	Bretherick 1979
Peroxyacetic Acid		•								•				Bretherick 1979
Potassium Permanganate		•											On heating	Bretherick 1979
Sodium Hydroxide	•						•						In a closed container	NFPA 1978
Sodium Peroxide		•											Explodes if warm	NFPA 1978

8.1 Compatibility of Acetic Anhydride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sulphuric Acid	•						•						In a closed container	NFPA 1978
Tetrafluoro-boric Acid	•												Very exotherm-ic reaction	Bretherick 1979
p-Toluenesul-phonic Acid		•											With water	Bretherick 1979
Water		•											Explosive if mineral acids present	NFPA 1978
CHEMICAL GROUPS														
Alcohols										•			Can react violently under certain conditions	Celanese PB 1978
Alkalis										•			Can react violently under certain conditions	Celanese PB 1978
Metal Nitrates										•				Bretherick 1979
Permanganates		•											Explodes if warm	NFPA 1978

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Acetic anhydride is a combustible liquid. Its vapours form explosive mixtures with air and may travel along surfaces to distant ignition sources and flash back (GE 1980; NFPA 1978). Acetic anhydride reacts exothermically with water.

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire. Water should be used sparingly because of the exothermic reaction (GE 1980; NFPA 1978).

Small fires: Dry chemical, CO_2.

Large fires: Alcohol foam, water spray (only if necessary).

Move containers away from fire area if this can be done without risk (ERG 1980). Avoid adding water inside containers (GE 1980).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (Celanese MSDS 1979). Water spray may be used to disperse the vapours and to protect men stopping the leak (GE 1980).

Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area and the contents transferred to other suitable containers (MCA 1962).

9.1.3.2 Spills on land. For small spills, absorb the liquid on vermiculite, dry sand or earth, and shovel into containers for disposal (GE 1980; NIOSH/OSHA 1981). The area can be covered with soda ash or sodium bicarbonate until cleanup (GE 1980).

For larger spills, contain if possible by forming mechanical barriers to prevent spreading. If possible, remove liquid with pumps or vacuum equipment. Neutralize remaining portion with lime or sodium bicarbonate.

9.1.3.3 Spills in water. Contain if possible. Neutralize with lime or sodium bicarbonate (EPA 670/2-75-042; OHM-TADS 1981). Activated carbon and Dowex 5WX4 should also be considered as sorbent materials in spill situations (CG-D-38-76).

9.1.4 Cleanup and Treatment.

9.1.4.1 General. For treatment of contaminated water, gravity separation of solids followed by neutralization with sodium hydroxide is recommended. Further treatment is accomplished by passing the above treated water through dual-media filtration. Any waste water from backwash of the filtration and adsorption units is returned to the gravity separator (EPA 600/2-77-227). Acetic anhydride can also be removed by treating the contaminated water with activated sludge (Metry 1980). Acetic acid is not removed appreciably by carbon treatment.

9.1.5 Disposal. Waste acetic anhydride must never be discharged directly into sewers or surface waters. Absorbed material or waste liquid can be burned in an approved incinerator. Use of an afterburner has been suggested for complete combustion (GE 1980). Following treatment, either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill.

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be acetic anhydride:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid acetic anhydride, where skin contact may occur (NIOSH/OSHA 1981).
- In tests of clothing materials, neoprene showed breakthrough times of about 1 hour; butyl rubber, PVC and Viton show breakthrough times of less than 1 hour (Little 1983).
- Splash-proof or chemical safety goggles are recommended for eye protection (NIOSH/OSHA 1981; Celanese MSDS 1979).

- Rubber is recommended for gloves, boots and aprons (GE 1980). Neoprene is also recommended for this application (Celanese PB 1978).
- The following chemical suit materials are recommended for protection against acetic anhydride (EE-20): neoprene, PVC (excellent resistance) and butyl (good resistance).
- Nonimpervious clothing which becomes contaminated with acetic anhydride should be removed immediately and not reworn until the acetic anhydride is removed from the clothing (NIOSH/OSHA 1981).
- Eye wash stations and chemical safety showers should be readily available in areas of use or spill situations (GE 1980).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where acetic anhydride is present (NIOSH/OSHA 1981; NIOSH 1978):

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapour concentration	
250 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapour cartridge(s).
	A gas mask with a chin-style or a front- or back-mounted organic vapour canister.
	Any air-supplied respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
1000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Fire fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapours. Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

9.1.7 **Storage Precautions.** Store in a cool, dry, well-ventilated area, away from sources of heat and ignition. Protect containers against physical damage. Acetic anhydride is incompatible with amines, alkaline materials and oxidizing agents (GE 1980).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 Explosion (Kirk-Othmer 1978)

A serious explosion occurred a number of years ago in the United States. A mixture of 568 L (150 gal.) of perchloric acid and 227 L (60 gal.) of acetic anhydride detonated. The explosion was very severe, killing 17 people and wounding many more. Several blocks were destroyed and 116 buildings in the area were completely demolished. This illustrates the reactivity of acetic anhydride.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Acetic Anhydride in Air

11.1.1 Colourimetric (NIOSH 1977). A range of 9.35 to 37.4 mg/m^3 (2.24-9.00 ppm) of acetic anhydride in air may be determined by bubbler collection followed by colourimetric determination.

A known volume of air is drawn through a fritted glass midget impinger containing 10.0 mL of hydroxylamine hydrochloride/sodium hydroxide absorbing solution. The absorbing solution is made in two stages. The hydroxylamine hydrochloride solution is made by dissolving 200 g hydroxylamine hydrochloride in 1 L of distilled water and stored in an amber container.

The sodium hydroxide solution is made by dissolving 200 g sodium hydroxide in 1 L of distilled water. The absorbing solution is prepared by combining equal volumes of the hydroxylamine hydrochloride and sodium hydroxide solutions.

The sample should be taken at a flow rate of 1 L/min. A sample size of 100 L is recommended. The sample is transferred to a 50 mL volumetric flask. The bubbler is rinsed with two 1 mL portions of distilled water and the washings added to the flask. A 5 mL aliquot of ferric chloride solution is added to the flask. The ferric chloride solution

is made by dissolving 100 g of ferric chloride hexahydrate in equal volumes of water and concentrated hydrochloric acid. The final volume should be 1 L. The volume of the sample in the 50 mL volumetric flask is taken to mark with equal volumes of hydroxylamine hydrochloride, sodium hydroxide and ferric chloride solutions.

The acetic anhydride is determined by reading the absorbance of the colour developed solution at 540 nm using 1 cm matched glass cells and a suitable spectrophotometer, in conjunction with a standard curve.

11.2 Qualitative Method for the Detection of Acetic Anhydride in Air

A range of 1 to 20 ppm of acetic anhydride may be determined using a Gastec detection tube for acetic anhydride. A known volume of air is drawn through a Gastec detection tube for acetic anhydride using a Gastec detector tube pump. A colour change from pink to dull yellow indicates acetic anhydride (Gastec).

11.3 Quantitative Method for the Detection of Acetic Anhydride in Water

11.3.1 Steam Distillation (AWWA 1981). Acetic anhydride may be determined as acetic acid in water. A range up to 5000 ppm of acetic anhydride as acetic acid may be determined by steam distillation.

A minimum volume of 1 L of representative sample is collected in an appropriate container and acidified to pH 3 with 50 percent sulphuric acid. A 6 mL volume of ferric chloride solution, prepared by dissolving 82.5 g ferric chloride hexahydrate in 1 L distilled water, is added to the sample.

A 50 g mass of diatomaceous silica filter aide is added and the mixture shaken. The sample is suction-filtered using a Buckner funnel containing a filter paper freshly coated with a thin layer of diatomaceous silica. The residue is washed four times with water and the filtrate adjusted to pH 11 with sodium hydroxide solution. The sample is concentrated to 150 mL on a steam bath and refrigerated. The cooled filtrate is adjusted to pH 4 with 58 percent sulphuric acid and transferred to a suitable distillation flask. Magnesium sulphate is added to slight excess and heat is applied to a steam generating flask connected to the distilling flask. A distillate volume of 200 mL is collected in approximately 25 min. The distillation rate is increased and 600 mL in total of distillate collected.

The acetic anhydride is determined by titration with 0.1 N sodium hydroxide using phenolphthalein indicator.

11.4 Qualitative Method for the Detection of Acetic Anhydride in Water

The sample is collected as in Section 11.3.1. One drop of sample is combined with 50 mg of solid sodium bicarbonate dissolved in 1 mL water. The mixture is shaken gently. Vigorous effervescence or steady gas evolution indicates a carboxylic acid (Owen 1969).

11.5 Quantitative Method for the Detection of Acetic Anhydride in Soil

11.5.1 Gas Chromatography (NIOSH 1977; ASTM 1979). Concentrations of acetic anhydride as acetic acid at the ppm level may be detected using a flame ionization detector.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar. Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract acetic anhydride from the soil. The Freon® is distilled from the reaction flask on a water bath at 70°C. Air is drawn through the flask for the final minute to remove all traces of Freon®. The residue is dissolved in carbon disulphide. A suitable aliquot of the dissolved residue is injected into a gas chromatograph equipped with a flame ionization detector.

The acetic anhydride is determined using an electronic integrator which measures the area under the peak in conjunction with a calibration curve.

Typical gas chromatograph operating conditions are: nitrogen carrier gas at 60 mL/min, hydrogen gas flow at 50 mL/min, air flow at 500 mL/min, injector temperature at 230°C, detector temperature at 230°C, and a column temperature of 130 to 180°C at 10°C/min.

11.6 Qualitative Method for the Detection of Acetic Anhydride in Soil

The sample is collected as in Section 11.5.1 and extracted using Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane). The Freon® is distilled from the reaction flask on a water bath at 70°C. Air is drawn through the flask for the final minute to remove all traces of the Freon®. The residue is dissolved in water. One drop of sample is combined with 50 mg of solid sodium bicarbonate dissolved in 1 mL of water. The mixture is shaken gently. Vigorous effervescence or steady evolution of gas indicates a carboxylic acid (AWWA 1981; Owen 1969).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_C	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_S	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_C	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight